

12-2010

Modeling Greenhouse Gas Emissions from Conventional Wastewater Treatment Plants in South Carolina

Andrea Hicks

Clemson University, akircho@clemson.edu

Follow this and additional works at: https://tigerprints.clemson.edu/all_theses

 Part of the [Environmental Engineering Commons](#)

Recommended Citation

Hicks, Andrea, "Modeling Greenhouse Gas Emissions from Conventional Wastewater Treatment Plants in South Carolina" (2010). *All Theses*. 989.

https://tigerprints.clemson.edu/all_theses/989

This Thesis is brought to you for free and open access by the Theses at TigerPrints. It has been accepted for inclusion in All Theses by an authorized administrator of TigerPrints. For more information, please contact kokeefe@clemson.edu.

MODELING GREENHOUSE GAS EMISSIONS FROM CONVENTIONAL WASTEWATER
TREATMENT PLANTS IN SOUTH CAROLINA

A Thesis
Presented to the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Masters of Science
Environmental Engineering and Earth Science

by
Andrea Lenart Hicks
December 2010

Accepted by:
Dr. Cindy Lee, Committee Chair
Dr. Shellie Miller
Dr. Mark Schlautman

Abstract

Wastewater treatment is an essential part of life in the urbanized world. As global climate change becomes a more pressing issue, the greenhouse gas emissions created through wastewater treatment will become a more prominent concern. Tertiary treatment will likely be standard for wastewater treatment plants in the near future, and therefore must be included in a model of greenhouse gas emissions. Also, the geographic location of a WWTP will change the mix of power types (e.g., coal, nuclear, biomass) used to run the plant. Although GHG emissions from the waste sector are small compared to the emissions of the United States as a whole, they should still be managed and reduced. CO₂e-WWTP, the model produced, is based largely on the work of Monteith et al. (2005) and was written using Visual Basic within Microsoft Excel to allow for a simple user interface. Modifications included removing a fitting factor for solids, generating a method for estimating the amount of nitrous oxide produced, and allowing for the calculation of greenhouse gas emissions from power from different sources. Eleven wastewater treatment plants, having capacities of 0.5 to 2.5 million gallons per day, were modeled for emissions of carbon dioxide, methane, and nitrous oxide. The plants were modeled with their current treatment systems and with the addition of tertiary treatment such as activated carbon, rapid sandfiltration, and an activated lagoon/wetland. The average carbon dioxide equivalent emissions for the treatment processes were found to be 0.410 g/L. It was found that in conventional wastewater treatment

systems that nitrous oxide production does not contribute significantly to overall greenhouse gas emissions (about 2-4% of carbon dioxide equivalent emissions), however, when solids treatment is considered nitrous oxide emissions are a more significant contribution (about 4-13% of carbon dioxide equivalent emissions). Several of the power sources created GHG emissions that were statistically different from the other power sources found through the use of an ANOVA. Greenhouse gas emissions from wastewater treatment processes and plants can vary greatly depending on the processes employed which is why CO₂e-WWTP is a valuable tool for those both in academia and the wastewater treatment field. However, more field research into wastewater treatment and its mechanisms for producing GHG emissions needs to be done.

Dedication

To Justin, for following me from Lake Superior to the Atlantic Ocean

Acknowledgements

Although this work only bears the name of one author, it would not have been possible without the help and guidance of numerous people along the way. First, I would like to acknowledge the wastewater treatment plants that provided the data for this model. Without them, end results would not have been possible.

I would like to thank my committee members Dr. Shellie Miller and Dr. Mark Schlautman for their suggestions and guidance along the way. I would like to thank my advisor Dr. Cindy Lee for encouragement on this project. But more importantly for taking me on as a graduate student and providing me with the tools to excel. And also for being willing to step out of her primary area of research and be my advisor. I would also like to thank the Clemson University Department of Environmental Engineering and Earth Sciences for the Teaching Assistantship, which allowed me to pursue my master's degree.

And finally I would like to thank my husband, Justin Hicks, who although had no formal role in this project served as a sounding board for all of my ideas. Without his encouragement and support this project would not have been possible

Table of Contents

Abstract.....	ii
Dedication	iv
Acknowledgements.....	iv
List of Tables	vii
List of Figures.....	x
List of Abbreviations	xi
Chapter 1	1
Literature Review	1
1.1 Current Research	1
1.2 Objectives of This Research	8
Chapter 2	10
Methods	10
2.1 Approach	10
2.2 Data Collection	11
2.3 Model (CO ₂ e-WWTP) Building	11
2.4 Primary Treatment.....	14
2.5 Primary Treatment Equations	15
2.6 Secondary Treatment.....	17
2.7 Secondary Treatment Equations.....	20
2.8 Tertiary Treatment.....	25
2.9 Tertiary Treatment Equations	28
2.10 Solids Treatment.....	29
2.11 Solids Treatment Example	31
2.12 Nitrogen.....	33
2.12.1 Wastewater Characterization	33
2.12.2 Current Guidance on N ₂ O Emissions	35
2.12.3 The Nitrogen Cycle	36
2.12.4 Nitrification.....	37
2.12.5 Denitrification.....	39
2.12.6 Fitting the N ₂ O Calculations to Realistic Data	46
2.12.7 Applicability Beyond Activated Sludge	48
2.12.8 Solids and Nitrogen	52
2.13 Greenhouse Gas Estimations.....	54
2.14 Power Estimations.....	55
2.14.1 Power Estimations Example.....	56
2.15 System Boundaries	64
Chapter 3	66
Results	66
3.1 Representative Raw Plant Data	66

3.2 Sensitivity Analysis	73
3.3 Similarity of Results.....	74
3.4 Overall Data and Analysis.....	75
3.5 System Optimization	84
3.5.1 Systems Parameters	86
3.5.2 Optimization Results and Discussion	91
Chapter 4	94
Discussion	94
Chapter 5	101
Conclusions and Recommendations	101
5.1 Conclusions.....	101
5.2 Recommendations	102
Appendices.....	104
Appendix A-Survey.....	104
Appendix B-Secondary Treatment Equations.....	106
Appendix C-Tertiary Treatment Equations	108
Appendix D-ANOVA Analysis	109
Appendix E-Solids Treatment Equations.....	110
Appendix F-Sensitivity Analysis	111
References.....	127

List of Tables

1	Primary Clarifiers Treatment Characteristics.....	15
2	Secondary Treatment Parameters.....	21
3	Tertiary Treatment Parameters.....	28
4	Parameters for Solids Treatment, Anaerobic Digestion	31
5	Variables for Anaerobic Digestion.....	32
6	Oxidation of Ammonia to Nitrite.....	38
7	Oxidation of Nitrite to Nitrate.....	38
8	N2O Activated Sludge Literature (Kampschuer et al., 2009).....	41
9	N2O Production(Adapted from Kester et al., 1997).....	42
10	Nitrogenous End Productsa(Adapted from Najjar and Allen, 1953).....	43
11	Distribution of Microbial Population (Heylen, 2007).....	43
12	Nitrogenous End Products per Genus.....	44
13	Weighting of End Products by Population.....	45
14	End Product Emissions Factors.....	46

15	N2O Fluxes from Full-Scope WWTP (Ahn et al., 2010).....	47
16	Power Usage (WEF, 1997).....	58
17	Carbon Based Power Impacts (Koch, 2000).....	60
18	Energy Sources and Usage for January 2010, United States and South Carolina (US EIA, 2010).....	62
19	Plant E Profile as Reported from the Survey.....	67
20	Effluent and Emission Data.....	68
21	N2O Expressed at CO2e.....	69
22	Energy Types and Their Impacts.....	69
23	Solids Treatment Emissions	70
24	Total CO2e Emissions for Solids Treatment.....	71
25	Grams of BOD and TKN Removed per Gram of GHG Produced.....	72
26	End Products.....	75
27	Overall Plant Data.....	77
28	Generalized Result Ranges.....	78
29	Generalized Wastewater Influent.....	81
30	Theoretical GHG Emissions from Standardized Influent.....	82

31	Comparison of Different Solids Treatments.....	83
32	Generalized WWTP Influent.....	85
33	Primary Clarifier Optimization.....	86
34	Ranges of Decision Variables for Optimization.....	87
35	Aeration Basin Optimization Parameters.....	87
36	Secondary Clarifier Parameters for Optimization.....	89
37	Optimized Effluent.....	91
38	Total Minimized GHG Emissions per Liter.....	92
39	Solution Set for the Relaxed HRT.....	93
40	US Waste-Sector CO ₂ e Emissions (Adapted from EPA, 2010).....	95
41	Carbon Cost of Treatment.....	99

List of Figures

1	Generalized Treatment Process.....	10
2	Overall WWTP GHG Emission Model.....	12
3	Primary Treatment.....	14
4	Secondary Treatment	18
5	Activated Sludge Process (Adapted from Monteith et al., 2005).....	20
6	Tertiary Treatment.....	27
7	Solids Treatment.....	30
8	The Nitrogen Cycle (Adapted from Colliver and Stephenson, 2000).....	37
9	N2O Activated Sludge Literature.....	42
10	Nitrogen Cycling in Wetlands (Adapted from Spieles and Mitsch, 1998)	50
11	Typical Distribution of Power Usage in WWTP (Metcalf and Eddy , 2003)	57
12	Total Power Generation in the US by Type.....	63
13	Total Power Generation in South Carolina by Type.....	63
14	System Bounds.....	64
15	Power Consumption Trend Based on Plant Capacity.....	79
16	GHG Trend Based on Plant Capacity.....	79
17	GHG Emissions Based on Influent Concentration.....	80
18	Expected GHG Emission Sources.....	85
19	Effects of Solids Treatment on Plant E Overall GHG Emissions.....	96

List of Abbreviations

Acid Ionization Constant.....	k_a
Aeration BOD Removal Rate.....	r_s
Aeration Rate of Basin.....	r_{O_2}
Ammonia.....	NH_3
Ammonium.....	NH_4^+
AN aerobic AMM onium O xidation.....	ANNOMOX
Biochemical Oxygen Demand.....	BOD
Biological Nutrient Removal.....	BNR
Carbon Dioxide.....	CO_2
Carbon Dioxide Equivalents.....	CO_{2e}
Cell Yield.....	Y
Concentration in Biomass Reactor.....	X
Concentration in Recycle.....	X_r
Cubic Meter.....	m^3
Days.....	d
Di-Nitrogen.....	N_2
Endogenous Decay Coefficient.....	k_d
Environmental Protection Agency.....	EPA
Greenhouse Gas.....	GHG
Grams.....	g
Hydraulic Retention Time.....	HRT
Intergovernmental Panel on Climate Change.....	IPCC
Kilogram.....	kg

Kilowatt-Hour.....	kWh
Kilowatts.....	kW
Liter.....	L
Methane.....	CH ₄
Methane Volatile Organic Compounds.....	MVOC
Milligrams.....	mg
Million Gallons per Day.....	MGD
Nitrate.....	NO ₃ ⁻
Nitrite.....	NO ₂ ⁻
Nitric Oxide.....	NO
Nitrogen.....	N
Nitrogen Dioxide.....	NO ₂
Nitrous Oxide.....	N ₂ O
Nitrogen Oxides.....	NO _x
Phosphorus.....	P
Rotating Biological Contactors.....	RBC
Solids Retention Time.....	SRT
Sulfur Dioxide.....	SO ₂
Total Kjeldahl Nitrogen.....	TKN
Total Suspended Solids.....	TSS
Visual Basic Editor.....	VBE
Volatile Suspended Solids.....	VSS
Waste Water Treatment Plant.....	WWTP

Chapter 1

Literature Review

1.1 Current Research

In the past the prevailing attitude in municipal wastewater treatment has been to treat the effluent water to the discharge standards regardless of the greenhouse gas (GHG) emission or energy consumption. The greenhouse gas emissions and power demand have often been considered immaterial compared to the necessity of treating the water to the discharge standards. However, that attitude has begun to change as other considerations, such as energy consumption, GHG emissions, and cost become increasingly important.

When GHG emissions have been modeled and/or quantified, the modeling has typically been for larger plants or very small specialized systems. In smaller systems the GHG emissions have generally been physically measured and not modeled. Examples of smaller systems include soil-trench wastewater treatment (Kong et al., 2002), swine farm lagoons (Vanotti et al., 2008), and constructed wetlands (Inamori et al., 2007). Additionally, none of the existing models that include data from operating plants were from the United States. This is notable due to the fact that wastewater treatment can vary on a country by country basis in terms of common practices for treatment and actual wastewater composition. The composition of the wastewater itself can vary among geographic areas.

Two approaches to modeling GHG emissions have been typical. The first approach was taken by Keller and Hartley (2003), where an idealized flow was used along with an idealized WWTP setup. The issue with this approach is that it is only done for one or two

possible plant set-ups and is only truly applicable to those hypothetical plants. The other approach for modeling GHG emissions was to fit a model to data from a limited number of plants (Monteith et al., 2005). A fitting term was used that was not constant for every plant and did not appear to have a physical basis. The fitting term employed was some fraction of the amount of solids going from primary treatment to secondary treatment. The example plant used to compare findings had a daily flow of 22,800 m³/day or about 6 million gallons per day (MGD). This plant and presumably the others to which the model was fit, are larger than the range considered in this work.

In both approaches, however, only methane (CH₄) and carbon dioxide (CO₂) emissions were modeled. The model created by Monteith et al. (2005) predicted a range of CO₂ emissions from municipal WWTPs determine GHG emissions of 0.077-0.349 kg of CO₂ per cubic meter (m³) of wastewater treated. In both cases the authors asserted that any nitrogenous emissions would be negligible. While one ton of CH₄ has the same global warming potential as 19.1 tons of CO₂, one ton of nitrous oxide (N₂O) has the same potential as 281 tons of CO₂ (EPA, 2009a). This means that even a small amount of N₂O emissions will have a large impact. N₂O emissions have been studied at one field site in Durham, NH (Czepiel et al., 1995). The study found that the plant produced 1.6*10⁻⁶grams of N₂O per liter of wastewater treated, which weighted in CO₂ equivalencies is equal to 4.5*10⁻⁴ grams of CO₂ per liter.

N₂O has recently been given more attention due to its large potential for impact. It was found in a recent study that N₂O emissions due to biological nutrient removal (BNR) can vary more than previously thought. In the past N₂O emissions have not been measured, and only occasionally modeled due to the fact that there was no consistent

protocol for measuring the emissions. This has led to the conclusion that poorly performing wastewater treatment plants (WWTPs) may be having a far larger impact on global climate change than was previously thought (Ahn et al., 2010). Additionally, N_2O has been found to be the most ozone depleting anthropogenic substance emitted (NOAA, 2009).

Industrial WWTPs have been only marginally studied in terms of their potential to emit GHGs. Typically whole processes have not been studied, but instead just a single unit within the process. The data from industrial WWTP modeling may or may not be helpful to municipal WWTPs, depending on the industry from which it was modeled. Industrial wastewater generally is at a higher strength and has greater concentrations of contaminants than municipal wastewater. Due to the higher strength there is the potential to emit more GHGs but also the potential to create more energy for plant use through burning the CH_4 generated. A study of the palm oil production industry in Asia found a CO_2 equivalent emission of 2.8-19.7 kg per kilogram (kg) of palm oil created (Reignders and Huijbregts, 2008). A study from Montreal created a model to estimate GHG emissions from industrial wastewater treatment. The GHG emissions from each process was estimated, however, there was no actual plant data used, just three different design configurations with assumed process parameters (Shahabadi and Haghighat, 2009).

Attempts have been made to quantify CO_2 equivalent emissions from large urban areas throughout the world. However, there is not a great deal of literature available on large urban wastewater treatment plants with respect to GHG emissions. A study by Rosso and Stenstrom (2008) was conducted; however, it was assumed that no N_2O was being produced. Rosso and Stenstrom (2008) assumed a theoretical treatment process

consisting of primary clarifiers, biological treatment, secondary clarifiers, and aerobic sludge treatment. The study, which did not provide many of the assumed parameters, found that proper treatment of wastewater in large urban areas is important in reducing the quantity of GHG emissions (Rosso and Stenstrom, 2008).

The current trend is that as more WWTPs are built, most of the plants will have the capacity for tertiary treatment (Metcalf and Eddy, 2003). Tertiary treatment is an advanced level of treatment with a goal of removing specific pollutants. It has been largely expected that many tertiary treatment process units will become part of conventional wastewater treatment in the next five to ten years (Metcalf and Eddy, 2003). Seeing as this reference is about seven years old, it would make sense that tertiary treatment would be fairly standard by now. In actuality a more correct prediction is that it would become standard in the next five years. It is currently standard on WWTPs in sensitive areas, such as the Chesapeake Bay. Tertiary treatment adds another level of treatment to the water, but in doing so also requires more power input.

As of 2004, there were 21,604 publicly owned municipal wastewater treatment plants in the United States (EPA, 2004). Of those, 16,388 reported flow data: 70% (11,564 plants) processed less than 0.5MGD, 17% (2,754 plants) processed between 0.5MGD-2.0MGD, and 13% (2,069 plants) processed more than 2.0 MGD. The target for model development in this thesis was plants that process between 0.5MGD and 2.0MGD, but the model can be adapted for different flow rates. This range was chosen due to the fact that plants of this capacity are likely to utilize conventional treatment systems but it is also probable that they do not have tertiary treatment yet.

Decentralized or satellite wastewater treatment has been suggested as an important segment of wastewater treatment as populations increase. These can range from small systems for a single household to larger systems for a small community (Levernz and Tchobanoglous, 2007). As of 2002 more than 60 million people lived in homes with decentralized wastewater management (Tchobanoglous, 2002). In some places, such as rural areas with low population densities and a great deal of open land, it is neither feasible nor cost effective to provide conventional sewer and wastewater treatment. Satellite systems typically involve reuse of the water locally, which will be important as the paradigm shifts from effluent water disposal to reuse, and from nutrient disposal to nutrient reuse (Levernz and Tchobanoglous, 2007). Although small decentralized treatment systems are an important portion of the wastewater treatment community, they are not included in this modeling system. The first reason that they are excluded is due to the fact that there has been a fair amount of research on very small and specialized systems. The second reason is that the focus of this study and model is to describe conventional and centralized wastewater treatment systems in the US, which have not been adequately modeled for GHG emissions.

Energy usage is an important aspect of wastewater treatment; as wastewater treatment becomes more complex, more energy will be required. In a study by Monteith et al. (2007) a mix of electricity generation for an industrial WWTP in Canada was analyzed in terms of the GHG emissions it would produce. The combination evaluated was 62.4% hydroelectric, 17.3% nuclear, 14.8% coal, and 3% gas. Each type of energy was then weighted with an emission factor of CO₂ equivalents per kilowatt-hour (kWh). The combination of energy sources is significantly different from the US mix. Most studies that

have considered energy usage in wastewater treatment are not current (e.g., Middlebrooks et al., 1981). Concern with energy usage has become more prevalent in recent years, with the societal shift towards conservation and consumption reduction. Additionally in the recent years the quantity of renewable energy sources has increased. Therefore, older studies are not necessarily applicable to today's WWTPs, as they are based on outdated consumption rates and power mixes.

Wastewater treatment yields not only clean water, but also a sludge comprised mainly of settled solids and organic matter. Houillon and Joliet (2005) conducted a study using data from WWTPs located in France to evaluate the effect of different sludge treatment processes in terms of GHG emissions and energy usage. The study used a hypothetical WWTP with theoretical influent characteristics along with theoretical sludge characteristics. The study took into account the energy usage to transport the sludge to the various treatment facilities and the GHG emissions associated with the energy usage. However, their approach can lead to the data being skewed, because the transport was greater for some processes, which made other processes seem more attractive in terms of GHG emissions, but the GHG emissions were not coming from the treatment process itself, but from transportation (Houillon and Joliet, 2005). The relevance of transportation in GHG emission analysis became apparent in the delineating of boundaries for the analysis reported in this thesis. Due to the ability of GHG emissions for transportation to skew the analysis, it is important that transportation be handled on a situation by situation basis. To accurately study the impact from the actual treatment process itself, transportation should be neglected.

Transportation has a large impact on results. One study conducted in France on wastewater sludge treatment that included transportation found that anaerobic digestion and land application had the lowest environmental impact (Suh and Rousseaux, 2001). However, the results from Houillon and Joliet (2005), also conducted in France, and also included transportation, were quite different. Incineration and agricultural use were found to have the lowest energy requirement, however, incineration in a cement kiln was found to be the best solution in terms of global climate change. Land filling and agricultural spreading were found to be the worst options in terms of global climate change. It is important to note that the terms land spreading and agriculture use of solids may be the same thing, but not necessarily. Land spreading may also include spreading of the solids for nonagricultural plant growth. Realistically, the impact of transportation is something that needs to be calculated for each treatment plant and end disposal option.

Energy has historically been predominantly produced in the United States through the burning of fossil fuels. The more energy required by wastewater treatment, the more fossil fuels burned, and consequently the more GHGs produced. Monteith et al. (2007) estimated the energy needed for wastewater treatment of different volumes and levels of treatment in Canada. The study, however, did not take into account the amount of GHGs produced in order to create the energy. It only accounted for the amount of energy used in WWTP but not the impacts of creating it.

Wastewater treatment is a necessary part of life. As more of the world becomes industrialized, the need for more efficient wastewater treatment will only become more urgent. By optimizing WWTPs, the water can be treated to higher standards using less energy, creating fewer GHG emissions, and potentially decreasing costs. Currently in the

United States, 82 % of the population is considered urban with an annual rate of change of 1.3% (CIA, 2010). The United States is already mainly an urban and industrialized country. But other countries, such as China with an urban population of 43% and an annual rate of change of 2.7% and Burundi with an urban population of only 10% but an annual rate of change of 6.8%, are becoming urban and industrial at a very rapid pace (CIA, 2010). People in urban areas live in closer quarters and at greater densities than people living in the rural sector; closer quarters necessitates wastewater treatment because septic and outhouse systems are no longer feasible, and not sustainable. Not only will more sustainable wastewater treatment be economically rewarding, but it will also contribute to less GHG emissions.

1.2 Objectives of This Research

The overall goal of this project was to investigate greenhouse gas emissions and energy usage at municipal wastewater treatment plants with flows of 0.5 -2.0 MGD. Following each objective is, in italics, some of the reasoning behind the choices of each objective.

The first objective was to create a model to estimate the greenhouse gas emissions based on user input about the influent, processing capacity, and design of the plant. The greenhouse gas emissions were then calculated and normalized to CO₂ equivalents on a per gallon treated basis. *Modeling the GHG emissions on a per volume treated basis allows for comparison of GHG emissions among treatment plants of different sizes.*

The second objective was to estimate the theoretical power usage of the plant and then compare it to the actual power usage of the plant, which allowed for comparison with

the value ranges from the literature. *It was important to estimate the theoretical power usage due to the fact that when additional treatment is modeled in conjunction with the current process design system, the original actual power data will no longer be valid.*

The third objective was to compare the greenhouse gas emissions with the power usage of the plant because it was assumed that there would be a correlation between the two. From the correlation or lack of correlation conclusions were drawn about optimal power sources. *As the world pushes towards “greener” energies it is important to be able to draw conclusions about their impact on traditional energy uses such as wastewater treatment.*

The fourth objective was to model a process treatment change and to evaluate how it affects the correlation between greenhouse gas emissions and power usage. This last objective was to demonstrate how the model can be used by practitioners but also researchers interested in improving the sustainability of wastewater treatment. *The real beauty of a model is that it is possible to reasonably approximate what may happen if a change is made without it actually being changed in the physical world.*

Chapter 2

Methods

2.1 Approach

The approach to accomplishing the objectives was to build a model, which from here forward will be referred to as “CO₂e-WWTP”, suitable for use by 0.5MGD to 2.0MGD plants. Data were gathered from several WWTPs in the upstate South Carolina region through the use of a survey. Based on a review of the literature, the most common processes in conventional wastewater treatment were included in CO₂e-WWTP. Suitable plants as determined from the returned surveys were evaluated by the model. CO₂e-WWTP was created using established standard parameters for different aspects of wastewater treatment, based largely on a study performed by Monteith et al. (2005) (Figure 1).

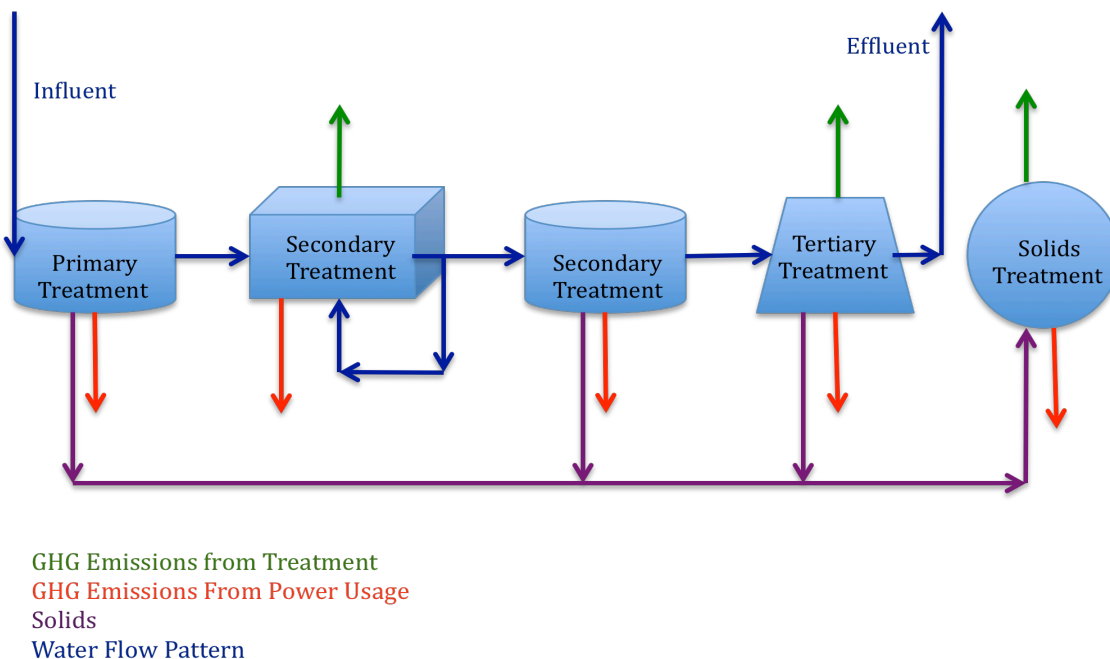


Figure 1: Generalized Treatment Process

2.2 Data Collection

A survey was created to collect data from wastewater treatment plants in South Carolina (Appendix A). The survey design allowed for the identification of the most common processes present in a mid-range conventional WWTP for the region. The survey design also allowed for the gathering of energy usage data. South Carolina as a southern state which has been growing more rapidly than other parts of the United States was an opportune place to survey. Due to its growth, the economy and the area have not been considered stagnant, and represent a developing area.

2.3 Model (CO₂e-WWTP) Building

The CO₂e-WWTP was built using Visual Basic Editor (VBE), which is a tool in Microsoft Excel, which allows for the building of macros. The idea was that an Excel file can be opened, parameters about the WWTP influent and treatment processes can be entered, and an estimation of the GHG emissions from the plant calculated. Excel was chosen because it is a readily available software package, and does not require purchase of a specialized piece of software. Considerable detail is provided in this section so that it can serve as a user manual.

Overall CO₂e-WWTP works by entering influent data for the plant, such as flow, biochemical oxygen demand (BOD), total suspended solids (TSS), phosphorus (P), and nitrogen (N) concentrations. A series of drop down tabs within the spreadsheet allow the user to select whether primary, secondary, or tertiary treatment is present (Figure 2). The GHG emissions are then calculated at each given level of treatment. After the GHG emissions are calculated for the current level, the remaining flow goes to the next

treatment level. If that treatment level is not present, then the flow proceeds directly to the next treatment level.

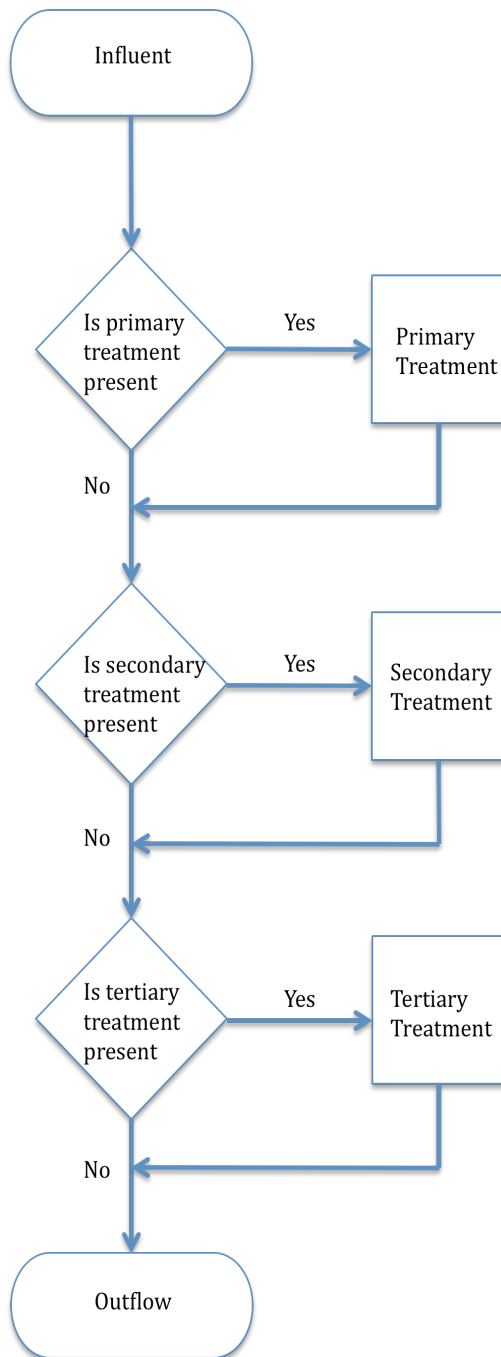


Figure 2: Overall WWTP GHG Emission Model

It has been suggested that carbon GHG emission rates can be calculated by utilizing a simple mass balance approach, such as all of the biodegradable carbon becoming CO₂ and creating solid waste only composed of inorganics (Monteith et al., 2005). This can lead to an overestimation of the CO₂ emissions from the wastewater treatment system. This suggests that although a mass balance can be utilized, it is important not to over simplify the situation. However, some of the carbon removed in a biological treatment plant would be sequestered in the biomass which is created by the microorganisms utilizing the carbon. Although some of the carbon may be respired or may endogenously decay, the majority will become biomass which is measured as a volatile suspend solid (VSS). VSS includes not only the carbon sequestered in the biomass, but other nutrients as well. The simple mass balance would not take into account the amount of carbon sequestered in the biomass. Therefore, this method can lead to an overestimation in terms of either CO₂ or CH₄ (Monteith et al., 2005). A parameter that has been used in literature is that 65% of the total suspended solids (TSS) are equal to the VSS (Monteith et al., 2005). TSS is the total amount of suspended solids, whereas VSS is the amount that can be oxidized at a temperature of 500±50°C, and is, therefore, assumed to be the organic portion. It is assumed that the VSS encompasses that organic portion of solids, although that is not always the case seeing as some organics will not burn and some inorganics break down at high temperatures (Metcalf and Eddy, 2003). Accounting for the solids that are removed during primary treatment is important, because those solids, typically thought to be the removed VSS, can yield GHG emissions as they decay.

2.4 Primary Treatment

Primary treatment typically consists of a primary clarifier or sedimentation basin, where solids fall out of suspension and where oils can be skimmed off, if necessary. Emissions of CO₂ and CH₄ can occur during primary treatment; however, these are generally unintentional products due to poor design or operation and are difficult to accurately predict (Monteith et al., 2005). Czepiel et al. (1995) found in a study performed in New Hampshire that the emissions of N₂O from primary treatment were negligible. Based on the work by Czepiel et al. (1995) and Monteith et al. (2005) CO₂e-WWTP does not model GHG emissions from primary treatment (Figure 3). Primary treatment does require some energy; however, it is about 10% of the total amount needed for treatment and transportation of wastewater in the plant (Metcalf and Eddy, 2003). Energy use has been included in CO₂e-WWTP in terms of calculating the GHG emissions produced by the various power sources for wastewater treatment.

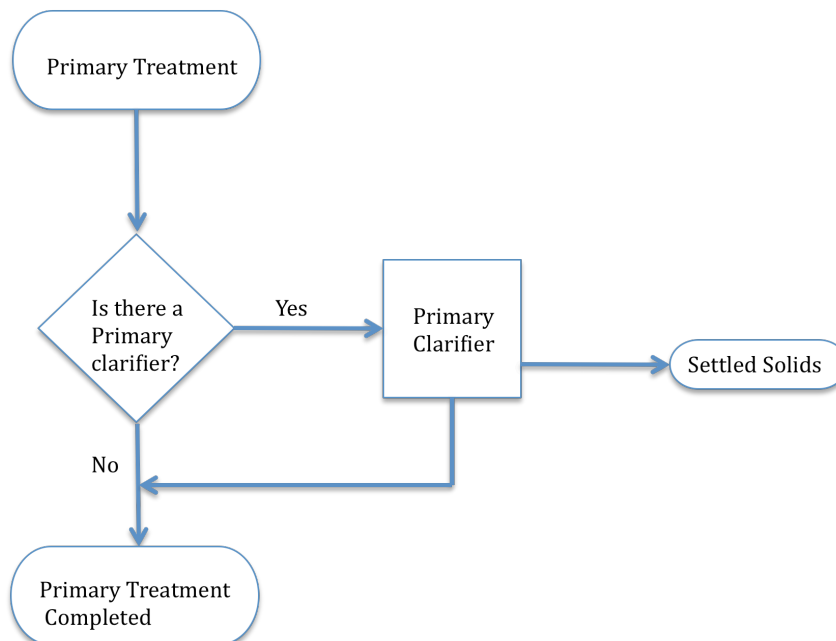


Figure 3: Primary Treatment

2.5 Primary Treatment Equations

Primary treatment typically consists of a primary clarifier, and for the purposes of CO₂e-WWTP, it is the only type of primary treatment considered. Primary clarifiers are not considered to produce GHG emissions unless they have been poorly designed and operated (Monteith et al., 2005; Bahgat et al., 1998). Therefore, the primary clarifier only affects what is transferred to the next treatment process and does not emit GHG emissions directly.

The primary clarifier was modeled using the same procedure as Monteith et al. (2005). The one major difference is that the amount of phosphorus and nitrogen being removed from the influent wastewater is being accounted for by CO₂e-WWTP (Table 1). It is important to note that the percentage removals that are listed here are not the only ones that can be utilized by CO₂e-WWTP. Alternate percentage removals may be entered into the Visual Basic macro. It is also important to note that there is no functional relationship hardwired in for the relationship of TSS paired with BOD removal. This could be added, but CO₂e-WWTP as utilized in this thesis uses the values shown in Table 1.

Table 1: Primary Clarifiers Treatment Characteristics

Wastewater Characteristic	Percent Removal	Reference
BOD ₅	25%	(Monteith et al., 2005)
VSS*	20%	(Monteith et al., 2005)
TSS	65%	(Monteith et al., 2005)
Nitrogen	20%	(Environment Canada, 2009)
Phosphorus	10%	(Environment Canada, 2009)
*Assuming that 65% of the TSS is VSS		(Monteith et al., 2005)

Using the above characteristics, several equations were generated to relate the influent water into the primary treatment with the effluent leaving the primary treatment. The terms labeled influent appearing in the equations below are necessary inputs to CO₂e-WWTP. The one exception is the *InfluentVSS*, which is calculated from the *InfluentTSS*.

$$InfluentVSS = (0.65) * InfluentTSS \quad (1)$$

$$VSSClarifier\ Removed = InfluentVSS * (0.2) \quad (2)$$

$$BODClarifier\ Removed = (0.25) * InfluentBOD \quad (3)$$

$$TSSClarifier\ Removed = (0.65) * InfluentTSS \quad (4)$$

$$NClarifier\ Removed = (0.2) * InfluentN \quad (5)$$

$$PClarifier\ Removed = (0.1) * InfluentP \quad (6)$$

Equations 1-6 allow the influent into the clarifier to be converted to the effluent leaving the clarifier and entering the next treatment step. If primary treatment is not present, then the influent concentrations would be the influent concentrations for the next treatment step. It has been noted that the portion of TSS that is VSS can vary within a range of 60-75%, although the value utilized here is 65% (Schalutman, 2010). As with any modeling endeavor most values utilized exist within an acceptable range, as does the one utilized here. Additionally, in typical primary clarifier design VSS removal is not considered a design objective; however, for the purposes of CO₂e-WWTP, it is necessary to track from one treatment step to the next.

2.6 Secondary Treatment

Secondary treatment involves treatment beyond physical treatment, such as biological or chemical treatment (Figure 4). The main goal is to remove biodegradable organic materials from the wastewater that would otherwise exert a demand for oxygen (O_2) in receiving streams or other water bodies. Unit operations for secondary treatment can vary greatly among WWTPs, due to the volume of water being treated and the different levels of BOD contained in the influent. Biological secondary treatment, such as an aeration basin and a trickling filter depend on bacteria to remove organic wastewater pollutants, thus creating biomass. As the biomass is formed and decays, there is the emission of GHGs. Non-biological secondary treatment processes also can be utilized such as floatation and flocculation. Flotation is a physical removal process whereas flocculation is utilized to increase the particle size of the pollutants so that they can be more easily settled out. Secondary treatment can, therefore, be a critical component when estimating GHG emissions and energy use because of the variety of processes that may be involved.

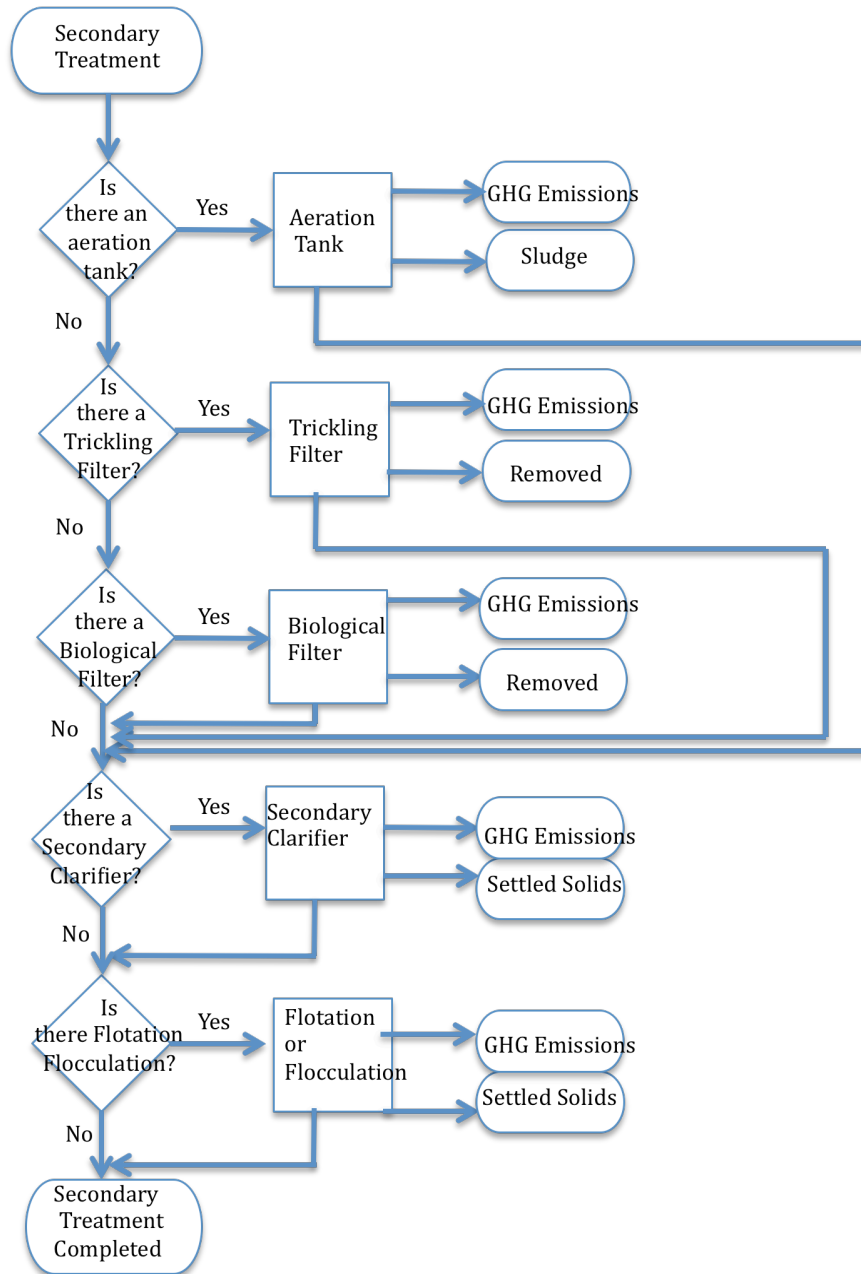


Figure 4: Secondary Treatment

Several options for secondary treatment are included in the estimation (Figure 4). As part of the user interface, drop down menus are included which allow for the selection of whether a plant has secondary treatment, and if so, what unit operations are included.

The equations for the aeration tank with sludge recycling are included in Section 2.7, and the equations for the alternative secondary treatments may be found in Appendix B.

In secondary treatment, GHG production can vary based on the method of treatment used. The GHG production values for each method of treatment were assigned from a combination of available literature and theoretical calculations.

Sludge is created through the settling of solids and biomass, which are important components due to the potential to emit large amounts of GHGs. Sludge holding tanks and aeration basins have been found to generate significant emissions of N_2O (Czepiel et al., 1995; Kong et al., 2002; Malhotra et al., 1964). In the study by Czepiel et al. (1995) secondary treatment consisted of four aeration tanks and two clarifiers, and significant emissions of N_2O were observed and measured. The amount of N_2O emissions is not, however, a straightforward calculation. The fraction of nitrogen that is emitted as N_2O has been shown to vary greatly, in the lab-scale between 0%-95% of the nitrogen load, and in full-scale between 0%-14.6% of the nitrogen load (Kampschreur et al., 2009). Currently the exact mechanisms for transformation of nitrogen to N_2O are unknown and a variety of data with contradicting results has been produced. The process of producing N_2O from nitrogen is performed by bacteria, and the dynamics of the bacterial communities are largely unknown. The currently accepted factor that is applied to wastewater treatment is 0.035% of the incoming nitrogen load will become N_2O (Kampschreur et al., 2009). That number comes from the conclusions of a single study by Czepiel et al. (1995), which found an emission factor of 3.2 grams nitrogen/person/year. However, more studies are necessary to verify the applicability of this rate. More detail on the formulation of the equations for the production of N_2O can be found in Section 2.12 below.

2.7 Secondary Treatment Equations

As illustrated above (Figure 4), there are many different types of secondary treatment. Development of the equations for activated sludge with recycle is described here, due to its prevalence in WWTPs. Aeration with or without recycle is the first option listed in Figure 4. Aeration with recycle as opposed to aeration without sludge recycling is illustrated due to the fact that it is one of the most common forms of secondary treatment. The procedure for modeling the secondary treatment process is similar to that employed by Monteith et al. (2005). There are some differences, however, in the procedure used here. Nitrogen loading and the subsequent production of N_2O was considered, which necessitated additional modeling. Below are the assumptions used to model the aeration basin with recycle portion of the secondary treatment process (Table 2).

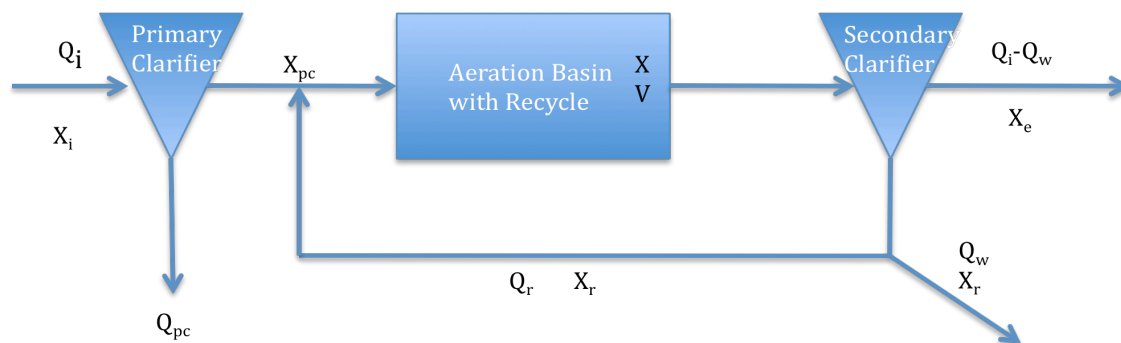


Figure 5: Activated Sludge Process (Adapted from Monteith et al., 2005)

It is important to note that the parameters that are listed here are not the only ones that can be utilized by CO₂e-WWTP. Alternate parameters may be entered into the Visual Basic macro.

Table 2: Secondary Treatment Parameters

Parameter	Value	Source
Hydraulic Retention Time (HRT)	6 hours	(Monteith et al., 2005 ^a)
Solid Retention Time (SRT)	5 days	(Monteith et al., 2005 ^a)
Biomass Concentration in Reactor (X)	1800 mg VSS/L	(Monteith et al., 2005 ^a)
Concentration in Recycle (X _r)	7500 mg VSS/L	(Monteith et al., 2005)
Ratio of BOD ₅ to BOD _u (f)	0.68	(Monteith et al., 2005 ^a)
Cell Yield (Y)	0.68 d	(Monteith et al., 2005 ^b)
Endogenous Decay Coefficient (k _d)	0.05 d ⁻¹	(Monteith et al., 2005 ^b)
Nitrogen Percent to N ₂ O	$\frac{4.03 * 10^{-7} \text{ gN}_2\text{O(TKN)}}{L}$	See section 2.12 for more information
Monteith et al., 2005 ^a , refers to sources used by Monteith et al. from Metcalf and Eddy 1991, also in agreement with Metcalf and Eddy (2003)		
Monteith et al., 2005 ^b , refers to sources used by Monteith et al. from WEF and ASCE 1998		

The following equations illustrate the relationships and transformations of the BOD and VSS within the secondary treatment system, particular to the activated sludge process of aeration with recycle.

$$V \left(\frac{dX}{dt} \right) = f_{nd} (Q_i - Q_{pc}) X_{pc} + YVr_s - Q_w X_r - (Q_i - Q_{pc} - Q_w) X_e - V k_d X \quad (7a)$$

$$YVr_s = Q_w X_r + (Q_i - Q_w) X_e = V k_d X + f_{nd} Q_i X_{pc} Y \quad (7b)$$

$$SRT = \frac{VX}{Q_w X_r + (Q_i - Q_w) X_e} \quad (8)$$

It is assumed that Q_{pc} , the sludge flow from the primary clarifier, is much less than Q_i , so that $Q_i - Q_{pc} = Q_i$. It is also assumed that steady state conditions can be applied, ($dx/dt=0$). These assumptions allowed for Equation 7a to be simplified to equation 7b.

V as seen is the volume of the reactor or in this case the aeration basin. Q_w is the fraction of the total flow that is being wasted in the aeration basin, which is due in part to the fact that this is an aeration basin with recycle, meaning that part of the sludge is being recycled back within the system. Q_i is the flow entering the basin; when the difference between Q_i and Q_w is taken, the flow leaving the basin with the effluent can be found. X_e is the concentration of the VSS present in the effluent, which represents not only the amount of VSS that entered the system from the prior treatment, but also the amount created in the process. X_{pc} is the concentration of VSS entering from primary treatment.

The assumption was made that the system was at steady state. This allowed equation 7 to be valid. It is important to note, that in the greenhouse gas estimation done by Monteith et al. (2005) a fitting factor (f_{nd}) was employed, ranging from 0.01 to 1, to more closely fit the results of the model to actual data. This fitting factor was defined as an adjustment for the fraction of VSS entering the aeration basin which has not been degraded. When no fitting factor was employed to test the sensitivity, the resulting GHG

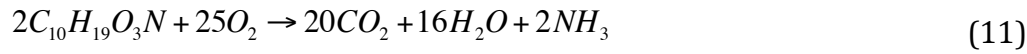
emissions for the carbonaceous compounds was about half of the values found by (Monteith et al., 2005). However, in CO₂E-WWTP no fitting factor was used, instead equation 8, which was utilized by Monteith et al. (2005), was modified to become equation 9 by the addition of the VSS leaving the clarifier and entering the secondary treatment.

$$X_e = \frac{\frac{V * X}{SRT} - Q_w * X_R}{Q_i - Q_w} + VSS_{in} \quad (9)$$

Once this was done, the carbonaceous GHG values approach the values found by Monteith et al. (2005) without the use of a fitting factor.

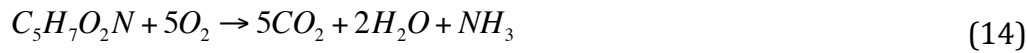
The following equations demonstrate the relationship of BOD removal and VSS removal/creation to the amount CO₂e emissions produced.

$$CO_2 = CO_2A + CO_2B \quad (10)$$



$$r_{o2} = V * r_s * \left(\frac{1}{f} - 1.42 * Y \right) \quad (12)$$

$$CO_2A = 1.1 * r_{o2} \quad (13)$$



$$CO_2B = 1.947 * V * k_d * X \quad (15)$$

The method used here for estimating GHG emissions from growth was adapted from Monteith et al. (2005). The treatment parameters can be seen in Table 2. As equation 10 suggests, there are two components to the CO₂ emissions from any sort of secondary

treatment growth process; the first (CO₂A) is the CO₂ released from the bio-oxidation of carbon contained in the substrate and the second (CO₂B) is from the endogenous decay of a portion of the biomass. As is illustrated by equation 11, carbon that has not become incorporated into the new biomass is typically converted to CO₂ aerobically. Assuming that BOD can be described by C₁₀H₁₉NO₃, the CO₂ emissions created can be estimated from the oxygen demand created through the conversion. Considering equation 11, and the molar masses of oxygen and CO₂, a rate of 1.1kg CO₂/kg O₂ can be found. The rate of oxygen utilization was found using equation 12; the result for $\left(\frac{1}{f} - 1.42Y\right)$ is 0.505 using the values in Table 2 and is unitless. From equation 13 the portion of CO₂ generated by the biological oxidation of BOD can be found. The second portion of the CO₂ emissions is due to endogenous respiration; a small portion of the biomass that has been created and incorporated into the solids is then respired. It is assumed that biomass can be represented by C₅H₇O₂N, and equation 14 can be used to represent the endogenous respiration. Using the chemical formula and the molar masses of biomass and CO₂, the CO₂ produced from endogenous respiration (CO₂B) is found to be 1.947 kg CO₂/kg biomass respired (equation 15).

$$r_s = \frac{(0.019 * Q_i * X_r) + [(Q_i - Q_w) * X_e] + (V * k_d * x) - (Q_i * VSS_{in})}{0.68 * V} \quad (16)$$

The r_s , which is the amount of BOD being removed in mg/day*liters, is then calculated. Then, multiplying it by the HRT allows the BOD removed to be found in mg/L, which allows the amount of BOD exiting the basin to be calculated. In the model presented

by Monteith et al. (2005) the VSS_{in} factor was not included. Including this factor transfers the amount of VSS entering from the primary treatment and incorporating it into the secondary treatment. When the VSS_{in} term is included and no fitting factor is used, then the carbonaceous GHG emissions are similar to the lower end of the range reported by Monteith et al. (2005).

2.8 Tertiary Treatment

Currently tertiary treatment exists at a limited number of WWTPs in the United States, but is by no means considered standard, although there are predictions that tertiary treatment will be standard in the near future (Metcalf and Eddy, 2003). Plants with tertiary treatment are typically in environmentally sensitive areas or have a particularly high load of a contaminant of concern. Tertiary treatment is generally a process selected or designed with an objective in mind. Examples of objectives for tertiary treatment include odor removal and nutrient removal (including nitrogen and phosphorus). Disinfection has been included in tertiary treatment due to its typical location in the treatment process; however, it is a required process component for WWTPs. Therefore it is not actually a tertiary treatment but a part of conventional treatment that would follow a tertiary treatment. Some common types of processes for tertiary treatment include activated carbon filtration, sandfiltration, and constructed wetlands. Typically tertiary treatment is considered as a “finishing step”, which is in addition to conventional treatment (primary and secondary), and thus requires additional power input. The general types of tertiary treatment include: sand filtration, activated carbon, lagoons/constructed wetlands, and specialized biological nutrient removal (Figure 6). Due to the variability of unit processes,

the GHG emissions and energy requirements are variable and must be calculated for each process.

It was expected that the South Carolina plants surveyed did not currently have tertiary treatment in place. The objective was to model what was currently emitted at the WWTPs, and then consider the addition of tertiary treatment and resulting emissions, based on the prediction that eventually tertiary treatment will be included in the majority of WWTPs in the US.

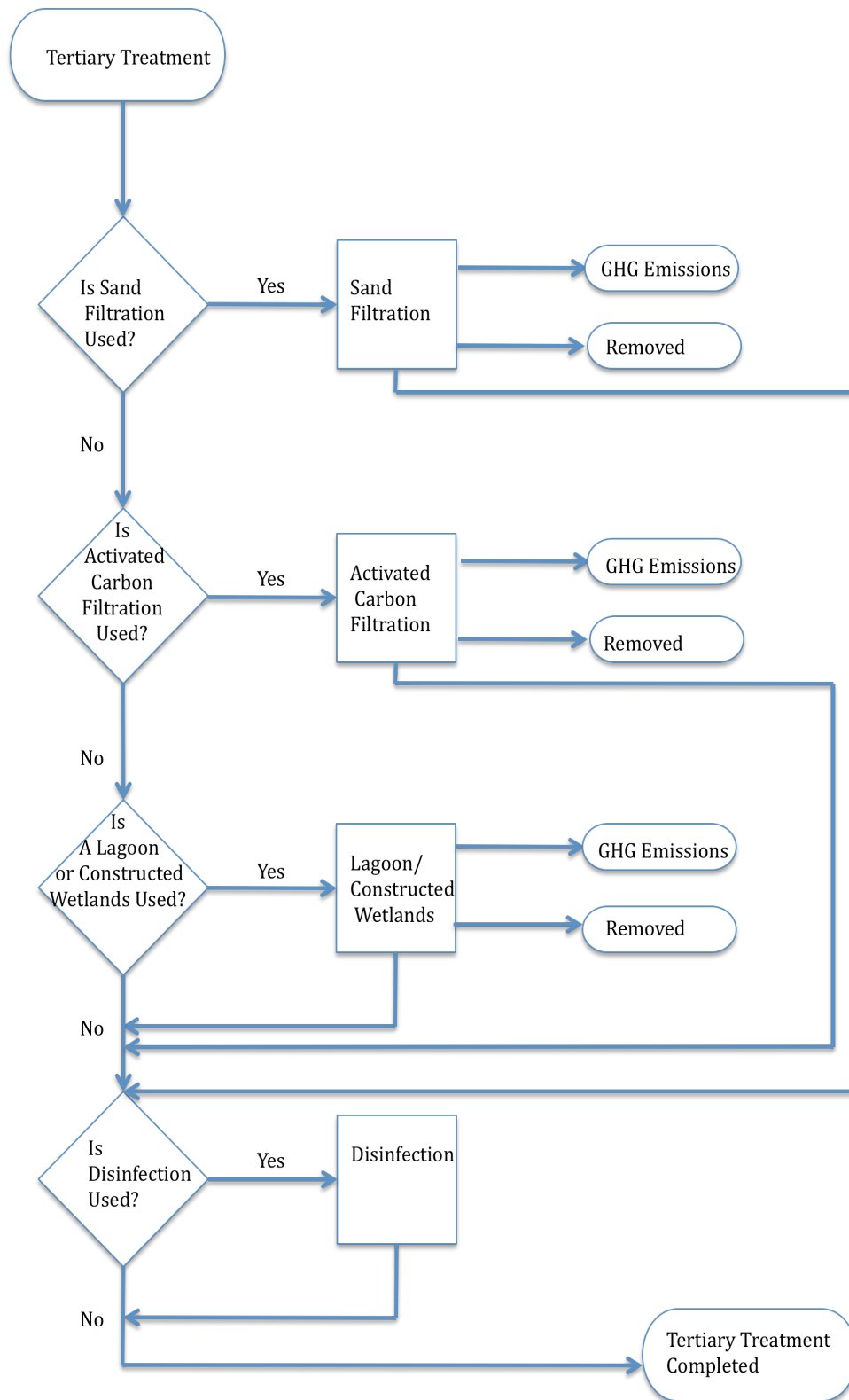


Figure 6: Tertiary Treatment

2.9 Tertiary Treatment Equations

The selected example for tertiary wastewater treatment is a treatment lagoon, because it was one of the few tertiary treatment processes modeled by Monteith et al. (2005); however, they only made it available as a secondary treatment option. Equations for the other processes within tertiary treatment are shown in Appendix C.

The assumed parameters are listed below (Table 3). The nitrogen end product and emissions modeling is further explained in section 2.12.

Table 3: Tertiary Treatment Parameters

Parameter	Value	Source
Hydraulic Retention Time (HRT)	120 hours	(Monteith et al., 2005 ^a)
Solids Retention Time (SRT)	5 days	(Monteith et al., 2005 ^a)
Biomass Concentration in Reactor (X)	200 mg VSS/L	(Monteith et al., 2005 ^a)
Concentration in Recycle (X _r)	1000 mg VSS/L	(Monteith et al., 2005 ^a)
Ratio of BOD ₅ to BOD _u (f)	0.68	(Monteith et al., 2005 ^a)
Cell Yield (Y)	0.68 d	(Monteith et al., 2005 ^b)
Endogenous Decay Coefficient (k _d)	0.05 d ⁻¹	(Monteith et al., 2005 ^b)
Nitrogen Percent to N ₂ O	$\frac{4.03 * 10^{-7} gN_2O(TKN)}{L}$	See 2.12 for more information
Monteith et al., 2005 ^a , refers to sources used by Monteith et al from Metcalf and Eddy 1991 Monteith et al., 2005 ^b , refers to sources used by Monteith et al from WEF and ASCE 1998		

Many of the parameters for the lagoon are the same as those for the aeration basin with recycle (Table 3). However, for a lagoon the HRT is longer than that of an aeration basin with recycle. The X concentration is much higher in a lagoon than for the activated sludge with recycle and the X_r is much smaller in a lagoon than in an activated sludge process. The other parameters remain the same. Equations 7-9 as described earlier in the paper were employed for the modeling of the lagoon.

2.10 Solids Treatment

The treatment of wastewater more often than not produces solids. The solids usually are treated in some manner to reduce their volume and mass to save disposal costs. There are several different options for the treatment of solids, ranging from anaerobic digestion to incineration to composting. For the purposes of CO₂e-WWTP, it was assumed that all of the CH₄ produced during anaerobic digestion was flared to CO₂. It is common practice currently to either flare the CH₄ or to burn it to heat the anaerobic digester. It is possible to generate electrical energy from the CH₄, but it is not common due to the large amount of permitting and paperwork required. CO₂e-WWTP could be used to approximate the amount of CH₄ that is generated from a wastewater treatment process, however at this moment it currently does not. In order for it to approximate the amount of CH₄ produced, the code would need to be changed to output the CH₄ values separately.

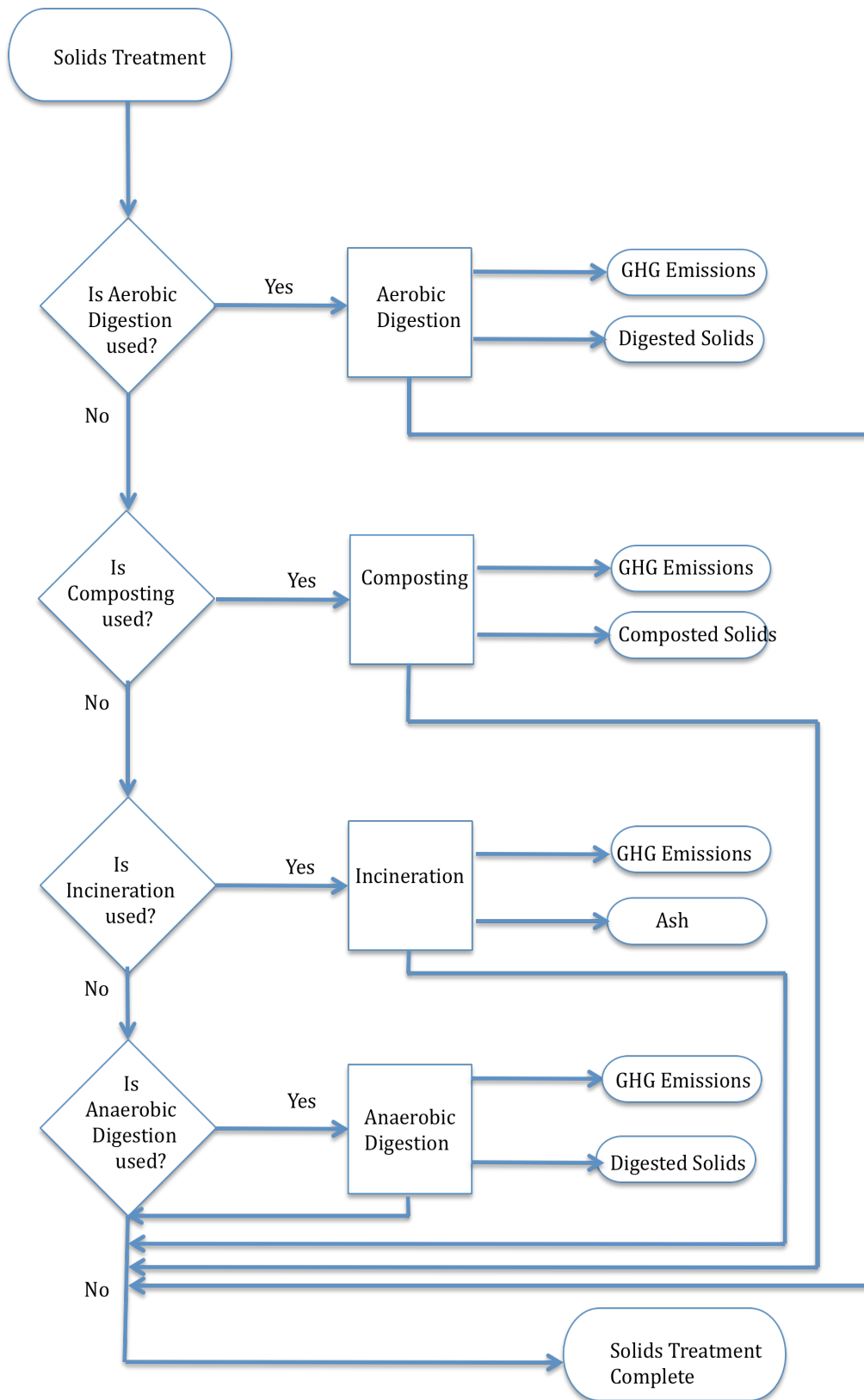


Figure 7: Solids Treatment

2.11 Solids Treatment Example

Anaerobic digestion was chosen from the processes modeled by Monteith et al. (2005) as the example for solids treatment, due to its potential to generate usable energy.

Table 4: Parameters for Solids Treatment, Anaerobic Digestion

Parameter	Value	Source
Pressure	1 atm	(Monteith et al., 2005)
Ideal Gas Constant	$8.21 \times 10^{-5} \text{ atm} \cdot \text{m}^3 / \text{mol} \cdot \text{K}$	
Percent Solids Reduction (PctRmv _{AN})	65%	(Monteith et al., 2005)
Volume CH ₄ Produced	65%	(Monteith et al., 2005, b)
Volume CO ₂ Produced	32%	(Monteith et al., 2005 b)
Volume of Biogas Produced per Gram of Volatile Solids Destroyed (GPR)	$0.9 \times 10^{-3} \text{ m}^3 / \text{g VSS}$	(Monteith et al., 2005 ^a)
Monteith et al ^a , refers to sources Metcalf and Eddy 1991		
Monteith et al ^b , refers to sources used by Monteith et al from WEF and ASCE 1998		

It is important to note that the parameters that are listed here are not the only ones that can be utilized by CO₂e-WWTP. Alternate parameters may be entered into the Visual Basic macro.

The following equations were used to calculate the amount and type of carbon based CO₂e emissions from anaerobic digestion.

$$\Sigma \text{Solids Produced} = M_{.xw} \quad (17)$$

$$VS_{\text{deg},an} = \text{PctRmv}_{AN} * M_{.xw} \quad (18)$$

$$BG_{\text{prod}} = GPR * VS_{\text{deg},an} \quad (19)$$

$$G_i = \frac{g_i * BG_{\text{prod}} * MW_i * P}{R * T} \quad (20)$$



Table 5: Variables for Anaerobic Digestion

Variable	Units	Meaning
M_{xw}	g VS/day	Grams of volatile solids produced per day
$VS_{deg\ an}$	g VS/day	Grams of volatile solids reduced by anaerobic digestion
BG_{prod}	m ³ /day	Volume of biogas produced
GPR	m ³ gas/g VS destroyed	Volume of biogas produced per gram of volatile solids destroyed
G_i	g/day	Production rate of biogas i by mass
g_i	unitless	Volumetric fraction of biogas that is made up of biogas i
MW_i	g/mol	Molar mass of gas i
P	atm	Pressure of biogas
R	atm*m ³ /mol*K	Ideal gas constant

Equation 17 sums all of the solids produced in the treatment processes. This would include solids produced from biological treatment and those collected in each of the clarifiers. Then equation 18 calculates the amount of volatile solids being reduced through anaerobic digestion. Note that the variables are defined in Table 5. From the amount of solids reduced, the amount of biogas produced is found using equation 19. Then, the amount of each biogas (CO₂ and CH₄) is found using equation 20, based on assumptions reported in the literature. It was assumed that all of the CH₄ produced is flared to CO₂,

using equation 21 and the assumption that 2.75 kg of CO₂ are produced per kg of CH₄ oxidized. In terms of GHG emissions and impacts, it is more environmentally responsible to oxidize CH₄ before releasing it into the atmosphere, versus just releasing it as CH₄ due to its much larger global warming potential. Some WWTPs do convert the CH₄ into electricity or use the heat generated by burning it to heat the digester. This is an advantage due to the fact that the energy or heat generated does not have to come from another source, but is instead salvaged from the GHG emissions produced by the WWTP.

2.12 Nitrogen

Nitrogen is important to consider when modeling wastewater treatment. Not only does it cause eutrophication in costal waters, but as N₂O, it has a very large global warming potential, when compared to that of CH₄ and CO₂. Unfortunately, at this time, there is a large amount of variability in measured and observed N₂O emissions from full-scale plants due to limited data being available (Ahn et al., 2010).

2.12.1 Wastewater Characterization

One common measurement for nitrogen concentration performed at WWTPs is total Kjehldahl nitrogen (TKN). The TKN is comprised of organic nitrogen, ammonia (NH₃), and ammonium (NH₄⁺). The inorganic portion of the TKN exists as either NH₃ or NH₄⁺ in the wastewater. Assuming that the activity of water is equal to 1, species exist in the following equilibrium equation (Metcalf and Eddy, 2003).

$$\frac{[NH_3][H^+]}{[NH_4^+]} = k_a \quad (22)$$

Typically in municipal wastewater approximately 40% of the TKN is organic nitrogen (EPA 2000), which leaves approximately 60% of the TKN as inorganic, composed of NH_4^+ and NH_3 . By assuming the acid ionization constant (k_a) is equal to $10^{-9.25}$ and that the pH of the wastewater is equal to 7, the above equation can be rearranged to find what portion of the inorganic TKN exists as NH_4^+ and what portion will be NH_3 .

$$0.60(TKN) = [\text{NH}_3] + [\text{NH}_4^+] \quad (23a)$$

$$\alpha_0 = \frac{[\text{NH}_4^+]}{[\text{NH}_4^+] + [\text{NH}_3]} = \frac{1}{\frac{[\text{NH}_4^+]}{[\text{NH}_4^+]} + \frac{[\text{NH}_3]}{[\text{NH}_4^+]}} = \frac{1}{1 + \frac{ka}{[H^+]}} = \frac{1}{1 + \frac{10^{-9.25}}{[10^{-7}]}} = 0.994 \quad (23b)$$

$$\alpha_1 = \frac{[\text{NH}_3]}{[\text{NH}_4^+] + [\text{NH}_3]} = \frac{1}{\frac{[\text{NH}_4^+]}{[\text{NH}_3]} + \frac{[\text{NH}_3]}{[\text{NH}_3]}} = \frac{1}{\frac{[H^+]}{ka} + 1} = \frac{1}{\frac{[10^{-7}]}{[10^{-9.25}]} + 1} = 0.00565 \quad (23c)$$

$$[\text{NH}_4^+] = \alpha_0 (0.60 * TKN) = (0.994) * (0.60) * (TKN) = (0.597) * (TKN) \quad (23d)$$

$$[\text{NH}_3] = \alpha_1 (0.60 * TKN) = (0.00565) * (.60) * (TKN) = 0.00339 * (TKN) \quad (23e)$$

Equation 23a illustrates the relationship that 60% of the TKN is assumed to be inorganic, which will be comprised of NH_3 and NH_4^+ . Equation 23b is utilizing the alpha to determine what portion of the overall inorganic nitrogen exists as NH_4^+ through the utilization of the assumed pH value and the pKa. As is evidenced by the solution, the majority of the inorganic nitrogen will be NH_4^+ . Equation 23c utilizes that alpha value and

confirms that the majority of the inorganic nitrogen will be NH_4^+ . Equations 23d and 23e give the portion of the TKN that will exist as each species of inorganic nitrogen.

In order for equation 23d and equation 23e to be utilized the TKN must be converted from a mass unit (mg/L) to a molar unit (moles/L). Since 60% of the TKN is inorganic and of the inorganic portion over 90% is NH_4^+ , it is assumed that the molar mass for NH_4^+ is a representative mass to use.

$$\frac{\text{mgTKN}}{L} * \frac{1\text{g}}{1000\text{mg}} * \frac{1\text{moleNH}_4^+}{18\text{gNH}_4^+} = \frac{5.6 * 10^{-5} \text{mole(TKN)}}{L} \quad (23f)$$

Equation 23f converts the TKN from mg/L to moles/L. This conversion allows the TKN to still be entered in mg/L, which are the commonly reported units, however, it changes the concentration into a value that can be applied with the alpha values.

2.12.2 Current Guidance on N_2O Emissions

The current modeling of GHG emissions from WWTPs has been largely focused on the carbon cycle and emissions in terms of carbon dioxide (CO_2) and methane (CH_4). There have been two main reasons cited for the neglect of the nitrogen cycle, the first being that whatever emissions produced are negligible and, therefore, insignificant (Keller and Hartley, 2003; Monteith et al., 2005). The second reason cited is that the mechanisms are still largely unknown, which is true. The second reason is far more valid than the first, since N_2O has approximately 300 times the global warming potential of CO_2 by mass, which means that even a very small amount will have a very large impact.

The current guidance of how to estimate N_2O emissions from WWTPs is set by the Intergovernmental Panel on Climate Change (IPCC) and is derived from a single study

(Czepiel et al., 1995). The estimated N_2O emission is 4 g N_2O /person, which is a multiplication of the emission factor generated by Czepiel et al. (1995) by 1.25, to account for industrial nitrogen loadings (Scheehle and Dorn, 2003). This factor is not based on the amount of wastewater treated but on the number of people served by the WWTP. This makes it less applicable to a given WWTP and flow. The guidance document by the Environmental Protection Agency (EPA) states that this factor has a great deal of uncertainty associated with it (EPA, 2010). The current method of estimating N_2O emissions is greatly limited, and necessitates more research (Ahn et al., 2010).

It has also been hypothesized that NO and N_2O emissions are higher than generally believed (Hiatt, 2006). It has been suggested that N_2O can be emitted in very non-negligible quantities during nitrogen removal (Kampschreur et al., 2009). The term non-negligible is utilized here to highlight that existing studies do not include N_2O emissions because they are considered negligible (Keller and Hartley, 2003; Monteith et al., 2005). This points to the need for a model that incorporates N_2O emissions. To do this, delving into the nitrogen cycle itself along with supporting microbiology is required.

2.12.3 The Nitrogen Cycle

Nitrogen is an abundant element on the surface of the earth. However, the element has a biogeochemical cycle whose mechanisms are not completely understood (Figure 8).

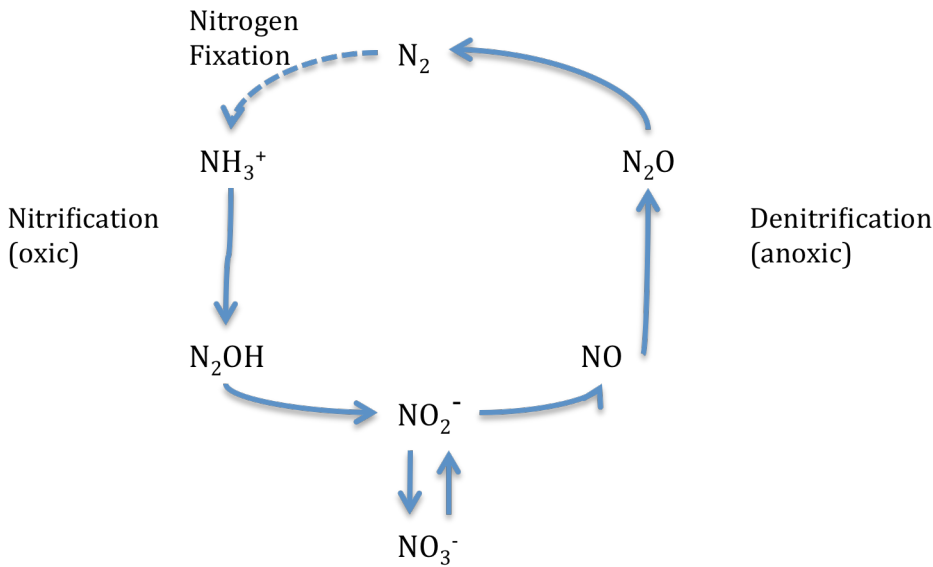


Figure 8: The Nitrogen Cycle (Adapted from Colliver and Stephenson, 2000)

In wastewater treatment there are two main parts to the nitrogen cycle. The first is nitrification where NH_3 is transformed aerobically to nitrate (NO_3^-). The second step is denitrification where the NO_3^- is transformed to a gaseous mixture of nitric oxide (NO), nitrous oxide (N_2O), and di-nitrogen or nitrogen gas (N_2) (Kakutani et al., 1980).

2.12.4 Nitrification

Nitrification is typically considered to be accomplished aerobically by *Nitrosomonas* and *Nitrobacter* genera of bacteria. The nitrogen is converted from NH_3 to NO_3^- (Colliver and Stephenson, 2000). The first step is the oxidation of NH_3 to nitrite (NO_2^-) (Table 6).

Table 6: Oxidation of Ammonia to Nitrite

Step	Reaction
1	$\text{NH}_3 + \text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{NH}_2\text{OH} + \text{H}_2\text{O}$
2	$\text{NH}_2\text{OH} + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + 5\text{H}^+ + 4\text{e}^-$
3	$0.5\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$
Total	$\text{NH}_3 + 1.5\text{O}_2 \rightarrow \text{NO}_2^- + \text{H}^+ + \text{H}_2\text{O}$

The second step is the oxidation of NO_2^- to NO_3^- (Table 7).

Table 7: Oxidation of Nitrite to Nitrate

Step	Reaction
1	$\text{HONO} + \text{H}_2\text{O} \rightarrow \text{HONO}_2 + 2\text{H}^+ + 2\text{e}^-$
2	$0.5\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$
Total	$\text{HONO} + 0.5\text{O}_2 \rightarrow \text{HONO}_2$

This gives an overall equation for the oxidation of NH_3 to NO_3^- .



Applying molar mass to the balanced overall equation 26, the amount of each component can be determined in reference to the TKN of the wastewater. This is also assuming that all of the NH_3 present is utilized in this reaction. Assuming a molar mass of 17 grams/mole for NH_3 , and that 56% of the TKN is NH_3 , the influent wastewater will have the following characteristics. TKN is expressed in mg/L.

$$\frac{\text{molNH}_3}{L} = \frac{1.87 * 10^{-7} (\text{TKN})}{L} \quad (27)$$

$$\frac{\text{molNO}_3^-}{L} = \frac{1.87 * 10^{-7} (\text{TKN})}{L} \quad (28)$$

$$\frac{gNO_3^-}{L} = \frac{1.20 * 10^{-5} (TKN)}{L} \quad (29)$$

All of these relationships are a function of the TKN measurement of the influent wastewater. This stoichiometric modeling, equations 27-29, gives an approximate amount of the NO_3^- available for denitrification.

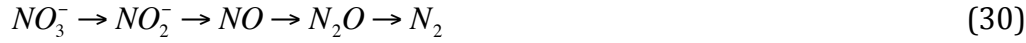
Additional organisms such as other bacteria, fungi, and algae that exist in wastewater treatment have been found to be able to carry out nitrification. However, they have been generally found to carry out nitrification only when the conditions are unfavorable to autotrophic denitrifiers, such as *Nitrosomonas* and *Nitrobacter* (Shiskowski and Mavinic, 2006).

2.12.5 Denitrification

Denitrification is typically thought of as an anaerobic activity with the facultative aerobes switching to nitrogen as a terminal electron acceptor in the absence of oxygen. Typical denitrifying microorganisms found in activated sludge include: *Alcaligenes*, *Pseudomonas*, *Methylobacterium*, *Bacillus*, *Paracoccus*, and *Hyphomicrobium* (Wagner et al., 2002). Of these, species of *Alcaligenes*, *Pseudomonas*, *Thiosphaera*, and *Bacillus* have been found to be able to denitrify under aerobic conditions (Huang and Tseng, 2001). However, the approach taken here for the estimation of end products will follow the convention that denitrification occurs mainly in the anoxic environment. But note, it has been shown to occur under a variety of conditions from fully aerobic to fully anoxic (Shiskowski and Mavinic, 2006).

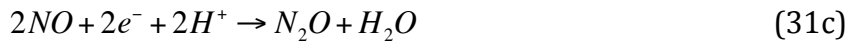
Unfortunately the exact mechanisms for denitrification are largely still unknown (Barford et al., 1999). However, it has been reported to date that the mechanisms have

much to do with enzymatic activity and gene expression (Yamaguchi et al., 2003; Heiss et al., 1989; Ye et al., 1995). In general the pathway of denitrification is considered to be consistent with the sequence below.



This representation makes it appear that the ultimate end product of denitrification should be N_2 and only N_2 . However, it has been shown experimentally that this is not the case (Najjar and Allen, 1953). Both NO and N_2O are also produced.

The individual denitrification reactions can be seen below (Heylen, 2007). It has been hypothesized, due to experimental observations, that the pathways and whether N_2O is an intermediate may be partially pH dependent (Thomsen et al., 1993). It has also been shown experimentally that some mutants of *Pseudomonas fluorescens* terminate with N_2O as their denitrification end product, and are not able to produce N_2 (St. John and Hollocher, 1977).



The fact that NO, N_2O , and N_2 are all often observed as end products during wastewater treatment suggests that the entire reaction is not always completed. The two main theories as to why N_2O is generated as an end product include carbon limitation and selective inhibition of the enzyme that converts the N_2O to N_2 (Shiskowski and Mavinic, 2006). There is a great variation in the amount of the different end products produced by

several in situ studies. The studies listed in Table 8 and Figure 8 are from full-scale activated sludge WWTPs, however, only the study by Czepiel et al. (1995) has been given much validity and has been widely applied. It is important to note that in each of these studies only one plant was studied; therefore, it is difficult to generalize about N₂O emissions from WWTPs.

Table 8: N₂O Activated Sludge Literature (Kampschuer et al., 2009)

% of N going to N ₂ O	Study
0.035%	(Czepiel et al., 1995)
0.600%	(Wicht and Beier, 1995)
0.001%	(Sumer et al., 1995)
0.020%	(Sommer et al., 1998)
0.080%	(Kimochi et al., 1998)
0.072%	(Schulthess and Gujer, 1996)

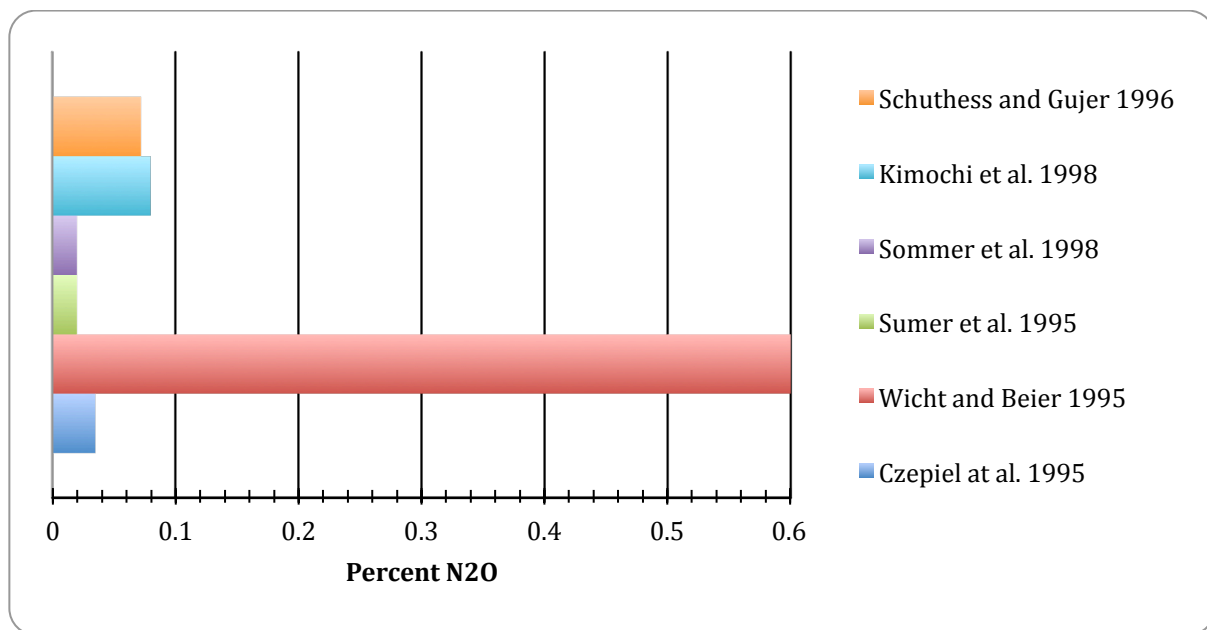


Figure 9: N₂O Activated Sludge Literature

The large differences in N₂O production (Tables 9, 10, and 11) may be due to the variation of microorganisms growing in different sludges. Not all denitrifiers produce the same quantities of each end product. Table 8 illustrates the large variance in N₂O emissions that has been observed across WWTPs and Tables 10 and 11 illustrate the different nitrogenous end products produced by different genera of bacteria found in WWTPs. It is worthwhile to note that in the earlier study (Najjar and Allen, 1953) that the starting point for their reaction was not NO₃⁻, but NO₂⁻. NO₂⁻ is a precursor step to the creation of NO₃⁻.

Table 9: N₂O Production (Adapted from Kester et al., 1997)

Microrganism	NO ₂ ⁻ %	N ₂ O %	N ₂ %
<i>A.eutrophous</i>	56.0	15.0	29.0
<i>P.stutzeri</i>	2.0	2.0	96.0

^aDenitrifiers were cultured in acetate-limited medium which contained 6 mM potassium acetate, 5 mM NH₄NO₃, 10 mM NaNO₃, 1 mM KH₂PO₄, 0.2 mM CaCl₂, 1 mM MgSO₄, and 0.1% (vol/vol) trace element solution.

Table 10: Nitrogenous End Products^a(Adapted from Najjar and Allen, 1953)

	N ₂ %	N ₂ O %	NO %
<i>P. stutzeri</i>	99.0	0.3	0.7
<i>B. subtilis</i>	70.0	20.0	10.0
^a The reaction mixture was composed of cell extract, 5.0 ml.; 0.3 per cent Difco yeast extract, 0.4 ml.; 1 M phosphate buffer, pH 6.7, 0.8 ml.; 0.1 M NaNO ₂ , 0.5 ml. Carbon dioxide was absorbed in 20 per cent KOH.			

One study (Table 11) cultivated the microorganisms from the activated sludge in a WWTP in order to better characterize their populations and presence (Heylen, 2007).

Table 11: Distribution of Microbial Population (Heylen, 2007)

Percentage of Population	Type
50.4%	Betaproteobacteria
36.8%	Alphaproteobacteria
5.6%	Gammaproteobacteria
2%	Epsilonproteobacteria
4%	Firmicutes
1 isolate of Bacteroidetes was also found	

The catalog is useful, because it presents a picture of what the microorganism population might be in a WWTP. Several of the genera listed above as commonly found in activated sludge fall into these categories: *Alcaligenes* (Betaproteobacteria), *Paracoccus* (Alphaproteobacteria), *Pseudomonas* (Gammaproteobacteria), *Bacillus* (Firmicutes). This

permits an assumption to be made that these genera are present in these concentrations. This is not exact, of course, but there is a great gap in research in terms of which bacteria and to some extent denitrifying archaea and fungi are present in WWTP (Heylen, 2007). It is also important to note, that the bacteria populations can easily vary regionally and according to the different constituents present in the influent.

Table 12: Nitrogenous End Products per Genus

Microbe	Mole NO per mole NO_3^-	Mole NO_2^- per mole NO_3^-	Mole N_2O per mole NO_3^-	Mole N_2 per mole NO_3^-	Source
<i>Pseudomonas</i>	-	0.20	0.010	0.480	(Kester et al., 1997)
<i>Alcaligenes</i>	-	0.56	0.075	0.145	(Kester et al., 1997)
<i>Pseudomonas</i>	0.07	-	0.015	0.495	(Najjar and Allen, 1953)
<i>Bacillus</i>	0.10	-	0.10	0.35	(Najjar and Allen, 1953)

As can be seen in Table 12 the two studies that investigated the nitrogen end product by *Pseudomonas* have very similar values. There were no values found for *Paracoccus* in the literature. Table 9 displays the different nitrogenous end products for *Pseudomonas* and *Alcaligenes*. It was indicated by Kester et al. (1997) that end products may change based on the amount of available oxygen. This illustrates that as the amount of available oxygen in the system changes so does the composition of the end products. Table 10 shows the findings of the end products from another study for *Pseudomonas* and *Bacillus*, which together with Table 9 allowed for the creation of Table 12 which illustrates the nitrogenous end products for the three genera shown.

A conservative approach to the approximation of the end products from *Paracoccus* would be to assume that they are very similar to *Pseudomonas*, which shows very little appreciable N₂O production compared to its other nitrogenous end products. These molar approximations of the end products can be applied to the approximate populations reported by Heylen (2007) in activated sludge.

Table 13: Weighting of End Products by Population

Percentage of the Total Microbial Population	Weighting Factor	Microbe	Mole NO per mole NO ₃ ⁻	Mole NO ₂ - per mole NO ₃ ⁻	Mole N ₂ O per mole NO ₃ ⁻	Mole N ₂ per mole NO ₃ ⁻	
0.504	0.510	<i>Alcaligenes</i>	-	0.56	0.075	0.145	1
0.368	0.372	<i>Paracoccus</i> *	0.07	-	0.015	0.495	1
0.056	0.057	<i>Pseudomonas</i>	0.07	-	0.015	0.495	1
0.04	0.041	<i>Bacillus</i>	0.10	-	0.10	0.35	1
0.02	0.020	<i>Epsilonproteobacteria</i> *	0.07	-	0.015	0.495	1
0.988	1						1
*No values were found; therefore, their values were referenced to the same as <i>Pseudomonas</i>							

Table 13 was created by combining the nitrogenous end products for each genus (Table 12) and the percentage of the microbial population that was composed of that genus from the study Heylen (2007) (Table 11). By analyzing the data presented in these tables relationships were generated in terms of what genus of microbes produce specific end products. A weighting factor can be found for each end product per mole of NO₃⁻.

$$NO \rightarrow [(0.372) * (0.07)] + [(0.057) * (0.07)] + [(0.041) * (0.10)] + [(0.020) * (0.07)] = 0.03553 \quad (32a)$$

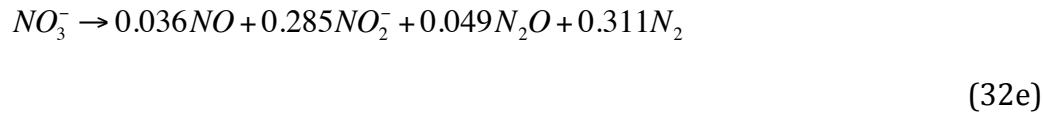
$$NO_2^- = (0.510) * (0.56) = 0.285 \quad (32b)$$

$$N_2O = [(0.510) * (0.075)] + [(0.372) * (0.015)] + [(0.057) * (0.015)] + [(0.041) * (0.10)] + [(0.020) * (0.015)] = 0.04908$$

(32c)

$$N_2 = [(0.510) * (0.145)] + [(0.372) * (0.495)] + [(0.057) * (0.495)] + [(0.041) * (0.35)] + [(0.020) * (0.495)] = 0.3105$$

(32d)



This allows the stoichiometric equations associated with denitrification to be applied to estimate the grams of each nitrogen end product per liter of water treated in terms of TKN (Table 14).

Table 14: End Product Emissions Factors

End Product	Emissions
NO₂⁻	5.33*10 ⁻⁸ mol NO ₂ ⁻ (TKN)/L
NO	6.73*10 ⁻⁹ mol NO (TKN)/L
N₂O	9.16*10 ⁻⁹ mol N ₂ O (TKN)/L
N₂	5.82*10 ⁻⁸ mol N ₂ (TKN)/L

The results suggest that although N₂ is still the predominant end product by mass and moles, the amount of N₂O produced is significant.

2.12.6 Fitting the N₂O Calculations to Realistic Data

Recently a study was completed evaluating and measuring N₂O emissions from 12 activated sludge WWTPs across the United States (Ahn et al., 2010). It suggested, as was mentioned before, that the current factor and estimation method for N₂O emissions from waste water treatment are not valid. Ahn et al. (2010) included WWTPs that include

biological nutrient removal (BNR). However, for CO₂e-WWTP it is assumed that BNR is not present, as it is not typically found in conventional wastewater treatment. BNR is a method of using growth and specifically designated oxic and anoxic zones to facilitate the removal of nitrogen from the wastewater. It is a form of tertiary treatment that should be considered if nitrogen is a constituent of concern in the wastewater. Due to the absence of BNR in the CO₂e-WWTP model, only the measurements in the study by Ahn et al. (2010) from WWTPs that do not have specific anoxic zones were considered (Table 15).

Table 15: N₂O Fluxes from Full-Scope WWTP (Ahn et al., 2010)

Plant Configuration	Temperature (°C)	Flow (MGD)	% Influent TKN emitted as N ₂ O	Low %	High %
Step-Feed Non-BNR A	26±0.81	93.0	1.8±0.79	1.10	2.59
Step-Feed Non-BNR B	30±2.3	2.0	0.24±0.02	0.22	0.26
Plug-Flow 1A	23±0.46	15.0	0.41±0.14	0.27	0.55
Plug-Flow 1B	11±0.41	8.7	0.62±0.15	0.47	0.77
Plug-Flow 2	22±0.58	6.6	0.09±0.03	0.06	0.12
Oxidation Ditch	19±0.58	3.4	0.03±0.01	0.02	0.04
Average				0.356	0.721

Using the the values from Table 15 for the plants without BNR, the lowest average for the percentage of TKN converted to N_2O is 0.356% and the highest is 0.721%. Combining the factors generated above (Table 14) with the results from Heylen (2007) predict that 0.043% of the TKN by mass will be converted into N_2O . The factor generated from the microbiological data is within the same order of magnitude as those values found by Ahn et al. (2010) for the Plug-Flow 2 and the Oxidation Ditch. This value is also consistent with several of the values found for the amount of nitrogen going to N_2O in other studies (Table 8).

Note the wide range of percentages of TKN converted to N_2O reported by Ahn et al. (2010) (Table 15). It has been stated in literature that many parameters such as solids retention time (SRT) and temperature are very important in determining the amount of N_2O emissions because they affect the distribution of microorganisms that are present. Different microorganisms favor different temperatures, SRT, and other parameters. The large discrepancy noted in the literature in terms of N_2O emissions is likely due to the differences among the microorganisms colonizing each activated sludge system.

2.12.7 Applicability Beyond Activated Sludge

The previously developed equations for N_2O production from activated sludge will be applied to trickling filter, rotating biological contactors, and lagoons/wetlands. They will not be applied to flotation/flocculation, activated carbon and disinfection. The rationale for these assignments is explained in detail below.

Trickling filters are generally considered to be aerobic, but also commonly have an anaerobic portion (Wik, 1999). In studies of the nitrification potential of trickling filters, it

has been found that the two nitrifiers common to activated sludge, *Nitrosomonas* and *Nitrobacter*, are also present in the trickling filters (Tal et al., 2003; Schramm, 2003). Along with this, many different types of fungus and algae are also commonly present (Cooke and Hirsch, 1958). There has been little study, however, into the microbial makeup of the denitrification population in trickling filters. Due to this lack of data, the denitrifying portion of the trickling filter will be assumed to be the same as the activated sludge.

Although some rotating biological contactors (RBC) have been designed for simultaneous nitrification and denitrification utilizing *Thiosphaera pantotropha* (Gupta and Gupta, 1999), it is assumed that this is not the case in most conventional WWTPs. RBCs treating wastes with very high nitrogen loading have been shown to have microorganism communities similar to **ANAerobic AMMONium Oxidation** (ANNOMOX). With these communities N_2 has been experimentally shown to be the major end product, with about 3% of the end product as N_2O (Pynaert et al., 2003).

RBCs have generally been considered aerobic environments, which would mean that unless some process such as ANNAMOX was occurring, that only nitrification and not denitrification would be occurring. This assumption, however, has been shown to be not entirely correct. RBCs have biofilms, which commonly have more than one layer, and each layer can have different characteristics. The top/outside layer of the biofilm is aerobic, which is where nitrification would take place. The deeper layers are typically anoxic, which is where denitrification would take place (Koch, 2000). The typical microorganisms associated with nitrification have been found in RBCs (Hitdlebaugh and Miller, 1981). However, little research has characterized the denitrifiers present; therefore, the

denitrifiers are assumed to exist in similar concentrations and genera as reported for activated sludge.

Wetlands are often used for tertiary treatment (Figure 10). Nitrogen removal can vary greatly from wetland to wetland, as well as from season to season. Generally when constructed wetlands are just beginning their life, they are inefficient at nitrogen removal, but as they age they can become more efficient (Spieles and Mitsch, 1998). Early nitrogen removal is accomplished mainly by the assimilation of the nitrogen to organic matter; an appreciable amount of organic matter must be present before denitrification will begin. There are many pathways for nitrogen removal within a wetland: mineralization of organic nitrogen, ammonia volatilization, assimilation into biomass, adsorption of ammonium onto substrate, and nitrification /denitrification (Spieles and Mitsch, 1998).

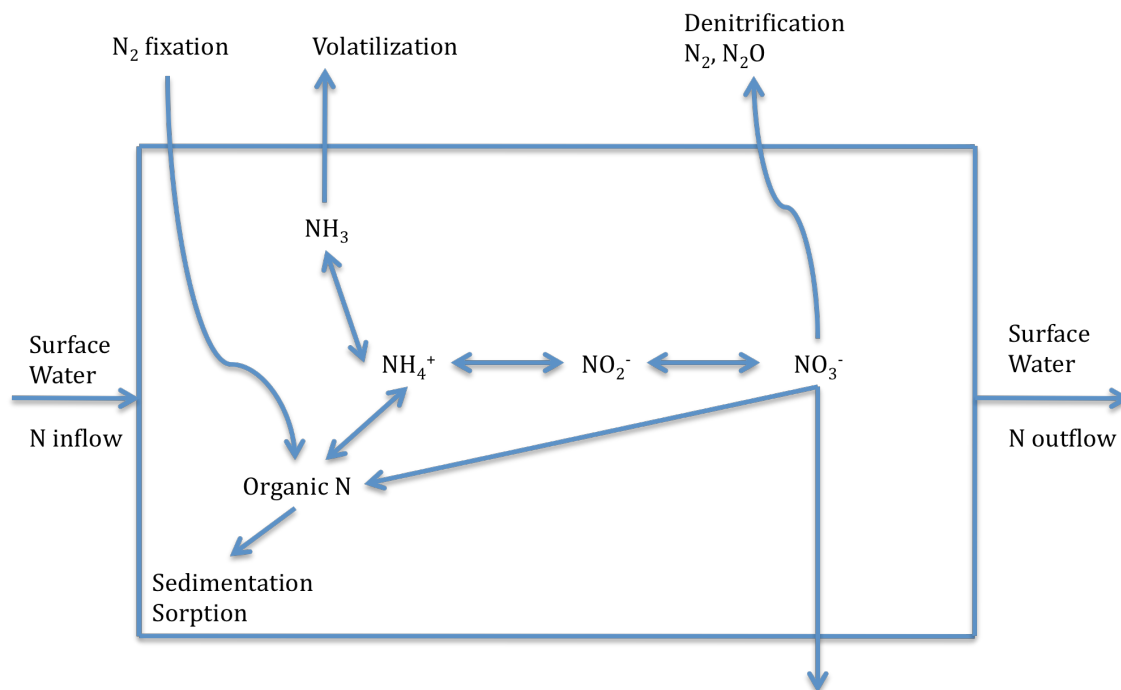


Figure 10: Nitrogen Cycling in Wetlands (Adapted from Spieles and Mitsch, 1998)

Although denitrifying bacteria exist in the water, they are more abundant in the soil (Brodrick et al., 1987). Plants and fungi can also take up nitrogen in the wetland system (Nichols, 1983). Disregarding what impacts the plants may have, due to the great variability in the type of nitrogen transformations that they catalyze, the microbiology is the key facilitator of nitrification /denitrification. However, due to a lack on literature on the characterization and distribution of the microorganisms present, the microbiological population is assumed to be similar in concentration and distribution as in activated sludge, which may not be an entirely valid assumption.

Lagoons are commonly used for tertiary wastewater treatment. The exact mechanisms of how nitrogen is removed and its form, however, are largely still unknown and debated. In some instances it has been observed that more N_2 is coming from a lagoon than can possibly be available by any known nitrification/denitrification pathway including Annamox, which leads to the conclusion that some other not yet known and understood process is occurring (Maynard et al., 1998). There has also been a large variation in the values for nitrogen removal reported in literature, which suggests that the parameters used to construct treatment lagoons are not complete. To an extent it has been debated whether nitrification/ denitrification play a significant role in nitrogen removal from lagoons (Maynard et al., 1998). Due to the lack of decisive literature on the topic, the lagoons will be modeled using similar characteristics to activated sludge.

Based on literature review there was no indication that flotation/flocculation, activated carbon processes or rapid sandfiltration have any impact on nitrogen gas production; therefore, these processes are assumed to not contribute to N_2O emissions in CO_2e -WWTP.

2.12.8 Solids and Nitrogen

Although nitrogen may be present in the solids that are being treated, that does not mean that all of the nitrogen present will be released from the solids or signify what form the nitrogen is in. Therefore, it is necessary consider each of the proposed solids treatment methods to determine what forms of nitrogen may or may not be released.

Before each individual type of solids treatment can be discussed, the make up of the solids in general must be considered. Generally the volatile suspended solids (VSS) can be described by the chemical formula $C_5H_7NO_2$ (Monteith et al., 2005). The total amount of VSS that is in the solids has been calculated in Section 2 on a per liter basis. Using this approach, the moles of VSS can be found, and consequently the mass of nitrogen in the VSS.

$$\frac{xVSSmgremoved}{LH_2Oprocessed} * \frac{1g}{1000mg} * \frac{1molVSS}{113gVSS} = \frac{molesC_5H_7NO_2}{LH_2Oprocessed} \quad (33a)$$

$$\frac{molesC_5H_7NO_2}{L} * \frac{1molN}{1molC_5H_7NO_2} * \frac{14g}{1molN} = \frac{gN}{L} \quad (33b)$$

The grams of nitrogen per liter from VSS give the total amount of nitrogen that will possibly be released. Nitrogen will be released only from the volatile portion of the TSS because the volatile portion is assumed to represent organic matter. TSS is operationally defined and contains both volatile and non-volatile components.

Anaerobic digestion (equation 34) is a common method of reducing the volume of sludge solids (Metcalf and Eddy, 2003).

$$\frac{gNsolids}{LiterH_2OTreated} * \frac{0.001gN_2O - N}{gNsolids} * \frac{1molN}{14gN} * \frac{1molN_2O}{2molN} * \frac{44gN_2O}{1molN_2O} = \frac{gN_2O}{LH_2OTreated} \quad (34)$$

The assumption was made that 0.001 g N₂O-N/g N in solids is the amount of N₂O released through anaerobic digestion (Vanotti et al., 2008). This factor was used in a study by Vanotti et al. (2007) modeling GHG emissions that included N₂O from anaerobic treatment of pig slurry due to the lack of data in conventional wastewater treatment. It is reasonable that some of the nitrogen will go to N₂O due to the oxygen contained in the solids themselves.

Aerobic digestion (equation 35) is another common way of reducing the volume of biosolids; however, unlike anaerobic digestion it is done in the presence of oxygen. Assuming that 45% of the VSS are removed/reduced (Monteith et al., 2005) the amount of nitrogen removed can be calculated.

$$\frac{gN_{solids}}{LH_2OTreated} * \frac{0.005gN_2O - N}{gN} * \frac{1molN}{14gN} * \frac{1molN_2O}{2molN} * \frac{44gN_2O}{1molN_2O} = \frac{gN_2O}{LH_2OTreated} \quad (35)$$

In this case, due to the abundance of oxygen, it is assumed that some of the nitrogen will be emitted as N₂O. It is assumed here that 0.005 g N₂O-N/g N solids of the nitrogen is emitted as N₂O, based on the work of Vanotti et al. (2008) that included aerobic digestion of pig slurry (Vanotti et al., 2008).

$$\frac{gN_{solids}}{LH_2OTreated} * \frac{0.005gN_2O - N}{gN} * \frac{1molN}{14gN} * \frac{1molN_2O}{2molN} * \frac{44gN_2O}{1molN_2O} = \frac{gN_2O}{LH_2OTreated} \quad (36)$$

Composting (equation 36) is another method for treating municipal wastewater solids. Composting has been defined as “an aerobic process of decomposition of organic matter into humus-like substances and minerals by the action of microorganisms combined

with chemical and physical reactions” (Peigne and Girardin, 2004). A similar value to that assumed for aerobic N_2O production was utilized due to the fact that composting is considered an aerobic process and insufficient literature exists on GHG emissions from composting.

Incineration is a method of treating solids, where the volume is greatly reduced by burning the solids to create ash. If stoichiometric combustion is assumed then N_2O is not an end product. It is generally assumed that all of the nitrogen will be released as N_2 although some may be released as NO or NO_2 (De Nevers, 2000). Therefore, it is assumed that N_2O is not released from incineration. Although N_2O could possibly be created during incineration if it is performed at adequate temperature this is not expected to occur (Svoboda et al., 2006). N_2O production increases during incineration as the temperature reached decreases (Svoboda et al., 2006).

2.13 Greenhouse Gas Estimations

The GHG emissions were estimated in each step of wastewater treatment on a per gallon treated basis. Normalizing the emissions to CO_2 equivalents per gallon treated allows for comparisons among treatment plants that are not the same size. In other studies GHG emissions have been normalized to units such as kg of CO_2 per m^3 of wastewater treated (Monteith et al., 2005) and grams (g) of N_2O per liter (L) treated (Czepiel et al., 1995). For this work, all of the emissions (CO_2 , CH_4 , N_2O) were converted into CO_2 global warming equivalents; one ton of CH_4 is equivalent to 19.1 tons of CO_2 and one ton of N_2O is equivalent to 281 tons of CO_2 (EPA, 2009a).

The GHG emissions were applied to the energy usage for both the current wastewater treatment configuration at each plant and then with added tertiary treatment. A calculator was created to estimate the GHG emissions for different combinations of power including coal, natural gas, nuclear, oil, hydrologic, wind, photovoltaic solar, and biomass.

2.14 Power Estimations

Power usage is an important, although often neglected issue, in the field of wastewater treatment. On the whole, the United States has been slower than the rest of the world to decrease their energy emissions. The White House's Global Climate Change Initiative allows for an increase of GHG emissions to 14% from 2000 levels, which is 54% higher than the commitment would have been under the Kyoto Protocol (Meier, 2002). The U.S. produces about one quarter of the world's anthropogenic GHG emissions, therefore Meier (2002) suggested it should take a leading role in the reduction of GHG emissions.

CO₂e-WWTP is flexible in terms of the input requirements for energy usage. Energy usage data can be entered based on historical plant consumption or the theoretical energy consumption of the plant can be calculated using established parameters if data are unavailable or as a check of actual usage. Theoretical energy usage is expected to be lower than actual energy usage due to the possibility of leaks or non-optimally performing equipment.

The contribution of power generation to GHG emissions is also calculated. Depending on the power source utilized the GHG emissions can vary. The model allows for different mixes of power sources to be used, ranging from nuclear, to coal, to biomass.

2.14.1 Power Estimations Example

The equations used to approximate the power usage of each process were scaled from values provided by WEF (1997) given for a typical 1 MGD plant (Table 16). If 1 MGD plant values were not available for a particular process, then the values were taken from the same process in the nearest size available. Assuming a linear relationship, the values were converted into kWh/liter of water treated. The flow of the plant being modeled is used to calculate the energy demand for each type of treatment being used. The power demand of all of the treatments being used is then summed and divided by the flow to create the number of kWh/liter treated for the entire plant. It is important to note that these power approximations do not take into account electricity use due to pumping through the plant, from one process to another. However, they do take into account pumping when it is utilized in specific treatment options like aeration with recycle, activated carbon, and rapid sandfiltration. All of these processes require pumping as part of the actual treatment step. Pipes and pumping are very dependent on the location, topography, and configuration of the WWTP, and for that reason have been omitted. The consequence of leaving pumping out of the power approximations means that the approximation of power usage and GHG emissions are lower than those that would actually occur. This could be significant if pumping makes up a large portion of the power demand at a WWTP; however, if it does not then likely the effects would be negligible.

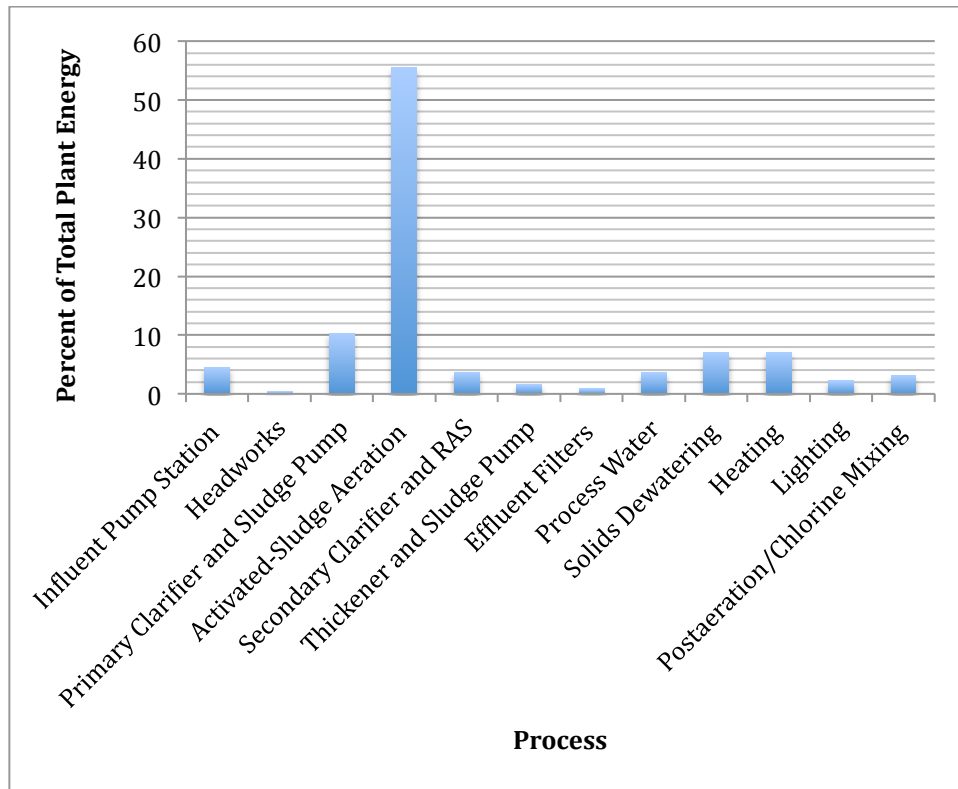


Figure 11: Typical Distribution of Power Usage in WWTP (Metcalf and Eddy , 2003)

In terms of a typical energy distribution for conventional secondary wastewater treatment the most energy intensive process by far is aeration for biological treatment, the second most energy intensive process is the primary clarifier and sludge pumping systems, and the third is treatment of solids and biosolids (Figure 11) (Metcalf and Eddy, 2003). WWTPs that have tertiary wastewater treatment typically require 30 to 50 percent more energy than conventional wastewater treatment. That said, pumping could increase the energy requirements causing the CO₂e emissions from them to be more significant.

Table 16: Power Usage (WEF, 1997)

Process	Plant Size	Energy Consumption
Primary Clarifier	1 MGD	15 kWh/day
Aeration with Recycle	1 MGD	577 kWh/day
Aeration without Recycle	1 MGD	532 kWh/day
Trickling Filter	1 MGD	352 kWh/day
Biological Filter (Rotating Biological Contactor)	1 MGD	1000kWh/day
Flotation/Flocculation	10 MGD	1805 kWh/day
Sandfilter ^a	1 MGD	352 kWh/day
Activated Carbon ^a	1 MGD	352 kWh/day
Lagoon	1 MGD	600-1400 kWh/day (average=1000 kWh/day)
Wetland ^b	1 MGD	600-1400 kWh/day (average=1000 kWh/day)
Disinfection (UV)	1 MGD	123 kWh/day
Aerobic Digestion of Solids	1 MGD	1000 kWh/day
Anaerobic Digestion of Solids	10 MGD	1100 kWh/day
Composting ^c	0 MGD	0 kWh/day
Incineration ^d		130-240 kWh/dry ton (Average=185 kWh/dry ton)
^a Data and values were not found for sandfilters or activated carbon, therefore the power requirement from a trickling filter was used instead		
^b Data was not found for Wetlands, therefore the power requirements from a lagoon were used instead		
^c It was assumed that composting is a largely natural process and that no additional power input would be needed		
^d Incineration power was calculated on a slightly different scale, in order to apply this to the solids, the assumption was made that the solids coming out of the treatment process are 3% dry solids by mass. (EPA, 2010)		

It has been logically suggested that as the complexity of a wastewater treatment system increases, so will its power demand (Monteith et al., 2007). In a study performed in Canada, Monteith et al. (2007) grouped WWTPs into variety of sizes ranges, from the very small (400 m³/day or 0.1 MGD) to the very large (200,000 m³/day or 52 MGD). Monteith et al. (2007) modeled energy consumption factors using design software and then compared the results to the actual energy consumption of WWTPs of similar size, using a variety of

configurations. The plant size considered in this thesis most closely corresponds to the small to medium plant range. In comparing the factors used here and by Monteith et al. (2007), some difference was observed. The energy usage in primary treatment for CO₂e-WWTP was found to be about half of the value found by Monteith et al. (2007). This result could easily be due to the fact that pumping was not taken into consideration; in primary treatment pumping can contribute up to 70 percent of the energy demand (Monteith et al., 2007). In terms of the activated sludge/aeration basin the results calculated by CO₂e-WWTP were slightly lower than those of Monteith et al. (2007). This could again be attributed to the omission of pumping, with pumping contributing up to 15 percent of the power demand in an activated sludge system according to Monteith et al. (2007). They also concluded that trickling filters, rotating biological filters, and lagoons all have similar power demand, in the range of 0.1×10^{-3} - 0.4×10^{-3} kWh/L treated. In comparison to the results of CO₂e-WWTP, RBCs, lagoons/wetlands all fall within the same power usage range. Trickling filters, however, exhibit a power demand that is far below those found by Monteith et al. (2007). Monteith et al. (2007) does not list what percentage of the power demand of a trickling filter may come from pumping; if it is a fairly large percentage that would easily compensate for the discrepancy between the power usage factor in CO₂e-WWTP and the one in the Canadian study.

The factors used to compute the GHG emissions in CO₂e are on a per kwh basis, which makes computing the GHG from power relatively simple (Table 17) (Koch, 2000). Different power sources have varying amounts of CO₂e emitted per the amount of power they generate. In South Carolina the majority of the power is generated using nuclear energy. But that is not true for the rest of the country (Table 20, Figures 12 and 13).

Although coal is largely the power source of the choice in the United States and to an extent South Carolina, that is not true for all regions (US EIA, 2010). Therefore several different power combinations were run to determine their impact on GHG emissions.

It is important to note, that although some energy sources emit lower amounts of CO₂e on a per kwh, there are other factors that are beyond the scope of this project that impact the environment. Some of these other factors include the disposal of spent nuclear waste, and the eutrophication impact of growing biomass to use for fuel. The values given in Table 17 include more than just CH₄, CO₂, and N₂O. The values for CO₂e also include sulfur dioxide (SO₂), nitrogen oxides (NO_x), non-methane volatile organic compounds (NMVOC), and particulate matter. These pollutants are emitted from different fuel sources, and although they have different environmental impacts, global warming is not one of them. These have human health impacts; however, these additional emissions do not have a direct effect on global climate change (EPA, 2009), and therefore are not included in CO₂e-WWTP.

Table 17: Carbon Based Power Impacts (Koch, 2000)

Power Source	g CO ₂ e range /kWh	Geometric Mean g CO ₂ e/kWh	Average g CO ₂ e /kWh
Coal	790-1,182	966.3	986
Natural Gas	389-511	445.8	450
Hydrological	2-48	9.80	25
Nuclear	2-59	10.9	31
Wind	7-124	29.5	66
Solar Photovoltaic	13-731	97.5	372
Biomass	15-101	38.9	58

Many of the power sources listed in Table 17 have large ranges. As can be seen, the geometric mean and the arithmetic mean of each power source are different. For the

purposes of the model the geometric mean was used because there were such large data ranges and the geometric mean by definition exhibits the tendency of the dataset. The geometric means of the fuel sources all fall within one standard deviation of the arithmetic mean with the exception of coal. This suggests that all of the power sources are statistically the same with the exception of coal.

However, to further confirm that validity of the assertion, a one-way ANOVA (analysis of variance) was run (Ott and Longnecker, 2001). From the ANOVA it is evident that the power sources are not statistically similar, because the F value of 400.41 is greater than the Fcrit value of 2.54 indicating that the hypothesis that all of the power sources are similar which was tested through the ANOVA must be rejected. Fisher's Least Significant Difference was performed which led to the conclusion that some of the power sources are statistically similar to each other (Appendix D). The South Carolina power mix by this method is considered statistically similar to biomass, coal, hydrological, nuclear, solar, and wind power sources along with the US power mix. The South Carolina power mix is considered not statistically the same as the natural gas power mix. This confirms that the test of whether the measurement fell within one standard deviation of the mean was not sufficient to determine statistically same values.

It is also important to note that when Koch (2000) calculated the generation of the CO_{2e} emissions for the power sources a life cycle approach was taken, which is why energy sources such as wind and solar have a GHG emission associated with them.

Table 18: Energy Sources and Usage for January 2010, United States and South Carolina (US EIA, 2010)

Energy Source	Amount US (10 ³ Mw)	Percentage of Total Power Generation US	Amount South Carolina (10 ³ Mw)	Percentage of Total Power Generation South Carolina
Coal	173,965	48.28	3,962	39.50
Nuclear	70,735	19.63	4,989	49.74
Hydroelectric	22,071	6.13	378	3.77
Natural Gas	72,600	20.15	548	5.46
Petroleum	4497	1.25	0	0.00
Biomass	4,659	1.29	146	1.46
Wind	4,659	1.29	0	0.00
Geological	1,350	0.37	0	0.00
Solar	1,063	0.30	0	0.00
Other	4,700	1.30	7	0.07
Total	360,299		10,030	

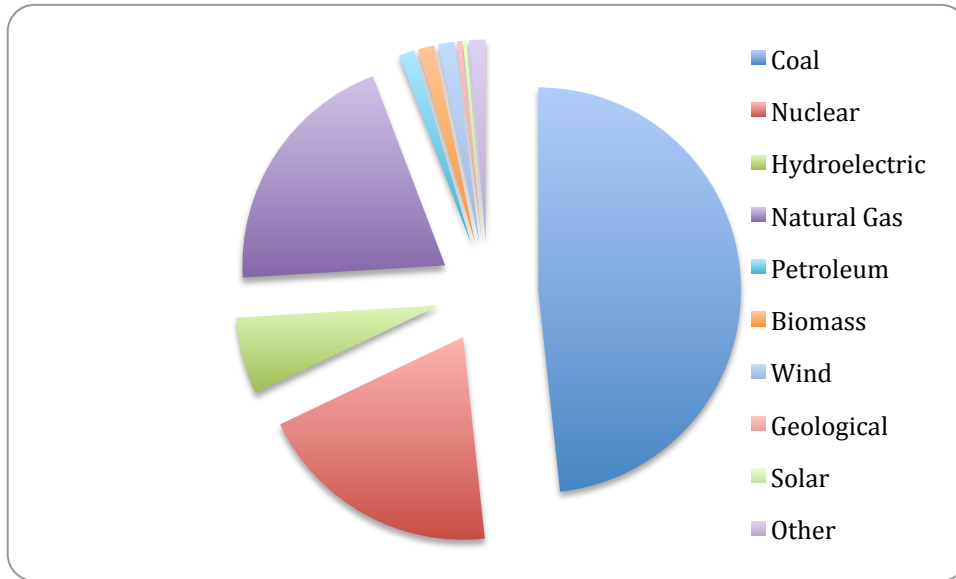


Figure 12: Total Power Generation in the US by Type

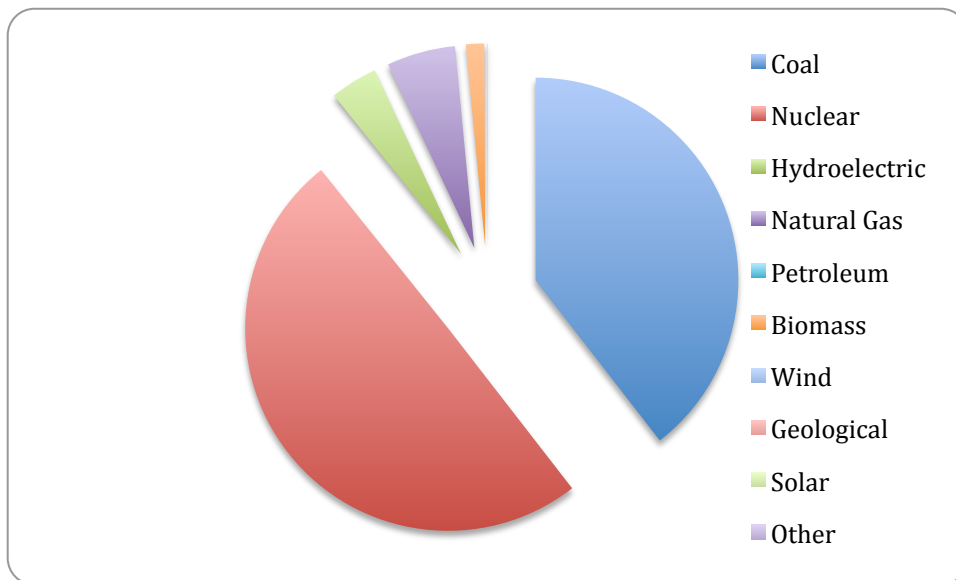


Figure 13: Total Power Generation in South Carolina by Type

Due to the large variety in power usage, several different power scenarios and combinations were run in CO₂e-WWTP. These included one similar to the power usage makeup of the United States (Table 18, Figure 12), one similar to the power usage makeup

of South Carolina (Table 18, Figure 13), and various others utilizing just one type of power source.

2.15 System Boundaries

For this study the system was bounded at the WWTP for treatment emissions (Figure 14). Certain emissions were not included such as CH₄ produced by land-filled sludge and emissions from land-applied sludge. If off-site emissions were included in the analysis, then emissions related to the transportation of the sludge would also need to be determined. Since transportation would vary from treatment plant to treatment plant, it has been omitted from this study. For purposes of this modeling study it was assumed that the incineration, composting, and digestion of solids were occurring on-site at the treatment plant.

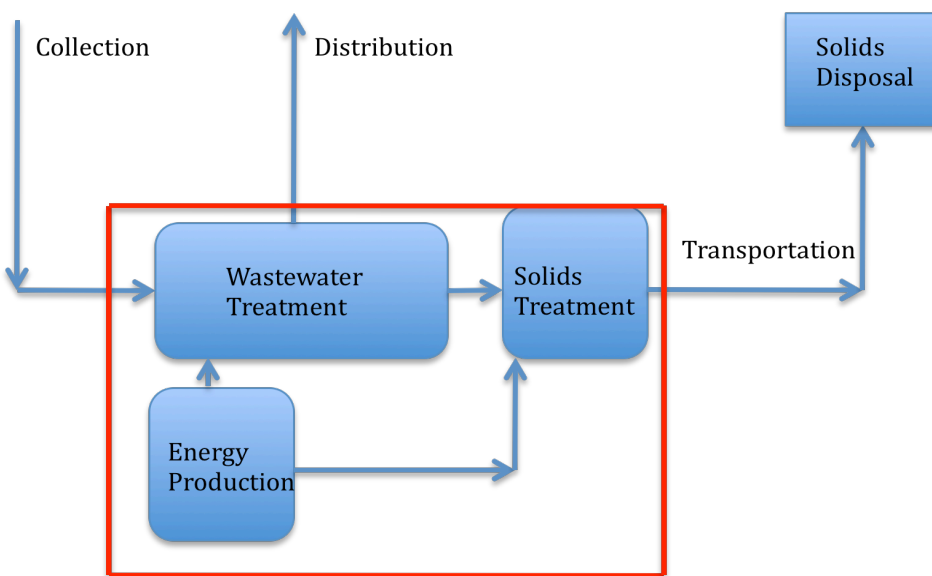


Figure 14: System Bounds

The neglect of transportation emissions can be justified by considering heavy-duty trucks, the type that would most likely be used to transport wastewater sludge. It has been found that 6.6 mpg (miles per gallon) is a reasonable assumption to make for the fuel efficiency of heavy diesel trucks (Huail et al., 2006). Using the Environmental Defense Fund “Fleet Greenhouse Gas Emissions Calculator”, (EDF, 2009), it was found that one gallon of diesel would produce 10.15 kg of CO₂ and 0.03 kg of N₂O. In CO₂e that would be 19.03 CO₂e, using the same global climate change conversion used for CO₂e-WWTP, which would lead to a value of 2.883 kg CO₂e/mile traveled. A factor this large could easily skew data if transportation was incorrectly included. Transportation is important in terms of quantifying total GHG emissions for waste water treatment; however, it needs to be evaluated on a plant by plant basis. A more appropriate time for this evaluation would be with a study on end of life options for waste waste sludge such as land application, landfilling, cement kiln, ect. Incorporating transportation in that regard would allow for better choices about the end of life facilities in terms of their distance away from the plant.

Some end of life options for the solids would also require an investigation into what is being displaced by their use. An example of this would be land application of sludge for fertilization purposes. Land application of the sludge would presumably replace conventional fertilizer usage, which could result in less GHG emissions. Trade-offs such as this would need to be fully evaluated.

The only off-site emissions that were included are those related to the power generation. These emissions are discussed in greater detail in Section 2.14.1 above.

Chapter 3

Results

The predominant use of a model such as CO₂e-WWTP is to generate results for both current and possible WWTP configurations. Results using data from a representative plant are examined in detail to demonstrate the utility of the model while averages are presented for all the surveyed WWTPs. As with all models, CO₂e-WWTP uses a set of equations and assumed values to generate possible results for both real and possible scenarios of WWTP schematics. A sensitivity analysis was performed to evaluate the sensitivity of the overall and unit process GHG emissions to several different parameters.

3.1 Representative Raw Plant Data

Although several plants were modeled and analyzed using the model, in the interest of time and space, only one complete example is shown. Average results from all the plant data are described in Section 3.4. The names and specific locations of the WWTPs will not be revealed due to the confidentiality of the surveys.

Plant E is located in South Carolina and its profile is shown below in Table 19. The disk filter shown in the profile is used to remove phosphorus. Because phosphorus was not tracked in CO₂e-WWTP, it merely represents an energy demand on the system. The plants surveyed were also asked for their monthly power usage, however, in many industrial settings power is not purchased by the amount used, but by the power capacity of the line running to the facility. For Plant E, the projected power usage from CO₂e-WWTP was 148,663.0 KW per month. It is necessary to mention that the energy projection does not

include any pumping, as the exact schematic for each plant was not known and is variable depending on layout and elevation.

Table 19: Plant E Profile as Reported from the Survey

Parameter	Value
Influent Flow	1 MGD
Monthly Power Consumption	N/A
BOD _{5IN}	182 mg/L
TSS _{IN}	320 mg/L
Nitrogen (TKN)	29.7 mg/L
Phosphorus	7.89 mg/L
Primary Treatment	Yes
Secondary Treatment	Yes
	Aeration tank with sludge recycling
	Secondary clarifier
Tertiary Treatment	Yes
	Disinfection
	Disk filter
Solids Treatment	Yes
	Aerobic digestion

The raw effluent and CO₂e data for Plant E are shown below. Unlike the study performed by Monteith et al. (2005), the end effluent values were not known for any of the plants modeled. Therefore, the effluent data displayed and analyzed for each of the plants, is not necessarily what their discharge is, but rather a prediction of what their discharge may be as projected by the model (Table 20). The results displayed below reflect only the CO₂e emissions from the actual processes, and not the GHG emissions generated by the power to run each of the processes.

Table 20: Effluent and Emission Data

Effluent	(mg/L)	From Treatment	CO ₂ e g/L	N ₂ O g/L
BOD	0	Secondary Treatment	0.164	9.74*10 ⁻⁶
TSS	46.5	Tertiary Treatment	0	0
VSS	30.2	Solids Treatment	0.143	1.20*10 ⁻⁴
TKN	20	Total	0.279	1.297*10 ⁻⁴

Different levels of the treatment system emitted different levels of GHG emissions. It was assumed that the primary treatment was well-designed so that no GHG emissions were emitted. The secondary treatment level produced 0.16 CO₂e grams per liter of water treated. As was shown in the plant profile the only types of tertiary treatment present were a disk filter for phosphorus and disinfection; it was assumed that neither of these processes produce GHG emissions directly. The solids were treated through aerobic digestion, and produced similar amounts of the GHG emissions with 0.14 CO₂e grams per liter of water treated to the GHG emissions from the conventional water portion. Approximately the same amount emissions were produced from the treatment of the solids compared to the actual treatment of the waste water. The N₂O emissions, which are included in the total GHG emissions, are also expressed directly as N₂O emissions (Table 21) and not as CO₂e. Although, when expressed directly as N₂O emissions and not in CO₂e the amount of N₂O emissions appear rather small, it is important to note that in order for them to be converted to CO₂e a multiplier of 281 must be applied, which means that the contribution of N₂O to the CO₂e for each level are much greater than they may appear (see Table 21).

Table 21: N₂O Expressed at CO₂e

From Treatment	N ₂ O g/L	N ₂ O Expressed in CO ₂ e g/L	N ₂ O percentage of CO ₂ e Total Emissions
Secondary Treatment	9.74*10 ⁻⁶	2.74*10 ⁻³	2.01%
Tertiary Treatment	0	0	-
Solids Treatment	1.20*10 ⁻⁴	3.37*10 ⁻²	23.6%
Sum	1.297*10 ⁻⁴	0.0365	25.61%

It is also interesting to note that although the total CO₂e generated through secondary and tertiary treatment are similar, the contribution of N₂O to their totals are different. For secondary treatment weighted N₂O only contributes approximately 2% of the overall CO₂e, whereas for solids treatment it contributes about 23%. This suggests that N₂O emissions may be significant for solids treatment.

The emissions due to the energy required by the current processes of Plant E were modeled using several different types of power, each with its own impacts. As is shown below (Table 22) the same process can have a wide range of GHG emissions depending on what fuel source was used. The South Carolina power mix produces less emissions than the United States power mix, although the difference is not a statistically significant amount.

Table 22: Energy Types and Their Impacts

	CO ₂ e g/d	CO ₂ e g/L
US Power Mix	1,189,293	0.315
SC Power Mix	856,240	0.227
Coal	2,006,323	0.531
Natural Gas	925,133	0.245
Nuclear	226,20	5.98*10 ⁻³
Hydro	20,337	5.38*10 ⁻³
Solar	202,334	0.0535
Wind	61,219	0.0162
Biomass	80,726	0.0214

When Tables 20 and 22 are compared, it can be seen that depending on the power source used the CO₂e emissions generated can be much greater than those produced by secondary treatment. When the US power mix was compared to the overall GHG emissions for Plant E, they were found to be on the same order of magnitude as the overall emissions. Which suggests that GHG emissions from power are a significant source of GHG emissions from conventional wastewater treatment. This suggests that for Plant E, power used to treat wastewater is equally important in terms of GHG emissions to the treatment process itself.

Solids treatment is often not thought of as a primary component of wastewater treatment, but as more of an afterthought in terms of how to reduce the volume of solids. However, the results from CO₂e-WWTP showed that treatment of solids can produce significant and variable GHG emissions; therefore they are worth analyzing.

The current treatment set-up of Plant E produces solids, which are treated by aerobic digestion. By varying the treatment of the solids the GHG can be reduced or increased. Table 23 shows the GHG emissions of various treatments applied to the solids generated by Plant E.

Table 23: Solids Treatment Emissions

	CO ₂ e, g/L (Solids Only)	N ₂ O, g/L (Solids Only)
Anaerobic Digestion	0.091	2.42*10 ⁻⁵
Aerobic Digestion	0.1429	1.20*10 ⁻⁴
Composting	0.0944	1.20*10 ⁻⁴
Incineration	0.2419	0

It was assumed the anaerobic digestion produced some CH₄ but that all of it was flared to produce CO₂. Although CH₄ may be used to generate heat for the digester or to produce energy, due to permitting complications this use was not assumed for the

purposes of this study. It was also assumed that no N₂O was produced from incineration due to the high temperatures reached by the solids in the incinerator. As can be seen above, there is not a large difference in the amount of GHG emissions between incineration and composting. Anaerobic digestion produced the smallest amount of GHG emissions per liter of waste water treated. Incineration, created the largest amount of GHG emissions. Aerobic digestion, which is a popular treatment, created an amount of GHG emissions that was in the middle of the range found.

However, changing the solids treatment also changes the overall power demand on the plant and thus the GHG emissions (Table 24). Determining the CO₂e emissions from power for the different solids treatment options was performed using a South Carolina power mix and theoretical power usage. As can be seen below, when the CO₂e emissions from power are added to those from treatment, aerobic digestion emerges as clearly the most potent type of treatment. Incineration, it is interesting to note, is a close second. Composting followed by aerobic digestion are the two lowest options in terms of total GHG emissions created for solids treatment.

Table 24: Total CO₂e Emissions for Solids Treatment

	CO ₂ e for Power Solids Treatment (g/L)	CO ₂ e for Power Total System	Percentage of CO ₂ e from Solids Treatment (Power)	CO ₂ e from Treatment g/L	CO ₂ e g/L from Solids Treatment and Solids Power Usage
Aerobic Digestion	0.109	0.227	48.09%	0.1429	0.252
Anaerobic Digestion	0.0120	0.130	9.24%	0.091	0.103
Composting	0	0.118	0%	0.0944	0.0944
Incineration	3.14×10^{-4}	0.118	0.266%	0.2419	0.242
No Solids	0	0.118	0%	0	0

CO₂e-WWTP can be used to evaluate trade-offs between BOD removed and GHG emitted. It is important to note, that by changing the functional unit from volume to grams of contaminant removal the results may be viewed in a different light. Typically in wastewater treatment the end goal is to remove pollutants to a satisfactory level. However, not all plants receive wastewater at the same strength, therefore a more applicable unit of measure to use is the mass of pollutant removed per mass of CO₂e produced. The model can be used to explore whether it is worth creating the additional GHG emissions from power in order to clean the effluent to a higher level (Table 25). As is seen below, the current treatment system with the SC power mix is the most efficient in terms of GHG emissions in removing BOD at 0.360 g BOD removed per g CO₂e. Although the tertiary treatment options do remove additional BOD, they do so at a high GHG cost per gram of BOD removed. For example, the lagoon option with the SC power mix removes 0.182 g BOD for every g of CO₂e. In terms of TKN removal the aerated lagoon/wetland system is the most efficient at 0.0256 g TKN per gram of CO₂e while the current system is predicted to remove 0.0182 g TKN per g CO₂e with the SC power mix.

Table 25: Grams of BOD and TKN Removed per Gram of GHG Produced

	US power (g BOD removed/ g CO ₂ e Produced)	SC power (g BOD removed/ g CO ₂ e produced)	US power (g TKN removed/ g CO ₂ e produced)	SC power (g TKN removed/ g CO ₂ e produced)
Current System	0.307	0.360	0.0163	0.0182
w/ Sandfilter	0.281	0.334	0.0150	0.0179
w/ Activated Carbon	0.260	0.309	0.0150	0.0179
w/ Lagoon	0.155	0.182	0.0219	0.0256
w/ Wetland	0.155	0.182	0.0219	0.0256

3.2 Sensitivity Analysis

Within any physical system, and particularly within a model there is often a range of acceptable parameters (Appendix F). It is important to evaluate the sensitivity of a model to certain parameters because engineers can take advantage of the knowledge to design physical systems that are more efficient. In the study by Monteith et al. (2005) ranges were given for many of the values used. As is noted in several of the previous tables, these ranges were obtained both from previous publications by Metcalf and Eddy and WEF. HRT, for example has a level of uncertainty which varies depending on the process that is being modeled. For conventional activated sludge, the HRT ranges from 3 to 8 hours. Six hours was used for modeling plant E and any other activated sludge processes present in this thesis. When the HRT is varied, the percent change in total CO₂e emissions for the treatment system ranges from -36.2 to 24.1%. However, HRT for lagoons and wetlands have a range of 72 to 210 hours, with 120 being the value chosen for modeling for the thesis. This large range, however, does not contribute to an equally large spread in GHG emissions, instead the percent change of CO₂e emissions falls between -21.6 and 54.0%. The greatest percent change was observed for the amount of VSS in the activated sludge basin. The acceptable range was very large, spanning 1100 mg/L to 6500 mg/L, with 1800 mg/L being the utilized value. This very large range resulted in the largest amount of change for CO₂e emission ranging from -22.3 to 131%.

For the thesis certain parameters such as HRT, SRT, and X were given assumed values. If the model is applied to a specific WWTP and the values for that plant are different from the assumed values in this model, those values can be entered into the model

in order to tailor the results to the plant. The survey used to gather information for this thesis did not request information on the assumed parameters, which was done to simplify the survey and increase the likelihood of it being returned completed.

The process for estimating N_2O emissions was developed as part of this project. There are no published ranges for the variables. When the parameter of the available NH_3 was varied the percent change of N_2O production varied from -0.098 to 0.147 percent. This yet again illustrates the need for more research in the area of N_2O emissions from wastewater treatment.

3.3 Similarity of Results

The carbonaceous GHG emissions determined by CO_2e -WWTP are similar to those found by Monteith et al. (2005). Without the use of a fitting factor the carbonaceous GHG emissions are slightly smaller than the range found by Monteith et al. (2005). The CO_2 emissions can be found using equations 10 through 16 and the processes described in secondary treatment.

Municipal wastewater typically has a TKN concentration in the range of 20-45 mg/L, whereas a combined wastewater and storm water system typically has a lower concentration of 4-17 mg/L (Metcalf and Eddy, 2003). For the purpose of testing the validity of this nitrogenous end products estimation procedure, an average of the municipal range was used of 32.5 mg/L. Assuming that 10% of the TKN is removed in primary treatment would yield the influent concentration of TKN to the activated sludge wastewater treatment as 29.25 mg/L.

Applying the equations listed in to this example yields the following end products shown in Table 26. As is seen below, the amount of nitrogenous emissions as N_2O is markedly less than the amount as N_2 .

Table 26: End Products

Product	Yield g/L
NO	5.91×10^{-6}
NO_2^-	7.17×10^{-5}
N_2O	1.18×10^{-5}
N_2	4.77×10^{-5}

3.4 Overall Data and Analysis

Forty-seven surveys in total were mailed to WWTPs within South Carolina, with addresses provided by the South Carolina Department of Health and Environmental Control (SCDHEC). A large list containing all of the WWTPs was provided by SCDHEC and through research the list was limited to the plants most likely to be in the targeted capacity range, 0.5-2.5 MGD, of this study. Of the 47 surveys sent out nine were returned as undeliverable by the postal office. Fifteen surveys were returned completed. Additionally, information was collected from three other WWTPs via email. Overall information from 18 WWTPs was collected and 15 of the plants were considered viable, which means that the present treatment is either conventional wastewater treatment or has a limited amount of tertiary treatment systems. Of the 15 viable plants, four were outside of the study range; those plants are highlighted in red in Table 27, which presents the current plant data. The WWTPs outside of the study range were not included in any of the overall results and characterizations. It is important to note here that several of the WWTPs did not provide

any data on their influent TKN concentration; for these plants, an assumed value of 32.5 mg/L was used, which is typical of a municipal influent value (Metcalf and Eddy, 2003).

Table 27 presents the results for all of the viable plants surveyed using the South Carolina power mix. The average CO₂e emissions from treatment alone are 0.224 g CO₂e/L for the 15 WWTPs within the target capacity range. The treatment combined with the power utilizing a South Carolina power mix averages 0.410 g CO₂e/L. It is important to note, however, that although the WWTPs fall within or near the boundaries of conventional treatment, they are not all using the same unit processes. There is a wide variation in the scale of the contribution of N₂O emissions to the overall CO₂e emissions among the plants. When the plants within the targeted size range are analyzed, it is apparent that the N₂O comprises 4-13% of the overall CO₂e emissions from treatment when aerobic digestion is used to treat the solids. When anaerobic or no solids treatment is present, then the N₂O emissions comprise only 2-4% of the overall CO₂e emissions.

Table 27: Overall Plant Data

Plant ^a	CO ₂ e g/L (Treatment)	CO ₂ e g/L (Treatment, Excluding N ₂ O)	N ₂ O g/L (Treatment)	Percentage of CO ₂ e from N ₂ O (Treatment)	CO ₂ e g/L (Treatment + SC Power Mix)	SC Power Mix, g BOD removed/ g CO ₂ e produced	SC Power Mix, g TKN removed/ g CO ₂ e produced
A (PC, AwR, SC, D, AND)	0.206	0.198	3.12*10 ⁻⁵	4.25%	0.298	0.784	0.0456
C (PC, AwR, SC, D, AD)	0.228	0.204	8.36*10 ⁻⁵	10.3%	0.416	0.567	0.0147
D (PC, AwR, SC, PF, D, AD)	0.224	0.201	8.36*10 ⁻⁵	10.5%	0.451	0.584	0.0223
E (PC, AwR, SC, PF D, AD)	0.279	0.243	1.30*10 ⁻⁴	13.1%	0.506	0.360	0.0200
F (PC, AwR, SC, D)	0.138	0.135	1.07*10 ⁻⁵	2.17%	0.217	0.876	0.0508
G (PC, AwR, SC, D)	0.136	0.133	1.07*10 ⁻⁵	2.20%	0.215	1.483	0.0485
H (PC, AwR, SC, D, W, AD)	0.484	0.464	6.99*10 ⁻⁵	4.06%	0.928	0.211	0.0312
I (PC, AwoR, SC, D, AD)	0.198	0.166	1.16*10 ⁻⁴	16.4%	0.382	0.589	0.0288
J (PC, AwR, SC, D, S, AD)	0.268	0.234	1.22*10 ⁻⁴	12.8%	0.494	0.405	0.0223
K (PC, AwR, D, AD)	0.209	0.189	7.16*10 ⁻⁵	9.63%	0.395	0.608	0.0218
L (PC, AwR, SC D)	0.137	0.135	1.07*10 ⁻⁵	2.19%	0.216	0.930	0.0509
M (AwR, D, SF, AD)	0.175	0.168	2.73*10 ⁻⁵	4.37%	0.362	0.249	0.0238
N (PC, AwR, D, AD)	0.212	0.191	7.40*10 ⁻⁵	9.80%	0.400	0.500	0.0275
Q (PC, AwR, SC, D, AD)	0.172	1.62*10 ⁻¹	3.56*10 ⁻⁵	5.83%	0.360	0.361	0.0170
R (PC, AwR, FF, D, AD)	0.297	2.58*10 ⁻¹	1.37*10 ⁻⁴	13.0%	0.504	0.298	3.97*10 ⁻⁴

^aPrimary Clarifier (PC), Secondary Clarifier (SC), Aerationwith Recycle (AwR), Aeration without Recycle (AwoR), Disinfection (D), Sulfite Filter (SF), Phosphorus Filter (PF), Sandfilter (S), Flotation/Flocculation (FF), Wetland (W), Aerobic Digestion (AD), Anaerobic Digestion (AND)

To determine averages for particular treatment types, similar plants were grouped. Only two processes, aeration with recycle and aerobic digestion, were shared by a significant number (>3) of the plants surveyed (Table 28). Aeration with recycle produced a very small amount of N₂O with the majority of GHG emissions coming from CO₂. It is important to note that the reason for the limited number of scenarios displayed below is due to the fact that only these two processes were present in three or more of the viable plants to allow generalized results. It is also important to note that some of the range in emissions for aerobic digestion can be attributed to the fact that not all plants are equally effective at removing solids.

Table 28: Generalized Result Ranges

Treatment	Range	Average	Standard Deviation
Primary +Aeration with Recycle+Secondary Clarifier (n=10)			
	CO ₂ e g/L	0.134-0.138	0.137
	N ₂ O g/L	1.94×10^{-7} - 1.31×10^{-5}	8.74×10^{-6}
Aerobic Digestion (n=8)			
	CO ₂ e g/L	0.035-0.162	0.106
	N ₂ O g/L	2.97×10^{-5} – 1.37×10^{-4}	8.97×10^{-5}

In terms of overall trends based on plant capacity there was found to be a strong correlation between the amount of power used and thus the GHG emissions from power (Figure 15). This is evidenced by the r² value of 0.82. However, in terms of GHG emissions from the treatment process there was no correlation with plant capacity (Figure 16). This is evidenced by the extremely low r² value of 0.0574. When the GHG emissions in

grams/liter for the treatment processes were compared with the influent TSS and BOD no correlation was found (Figure 17).

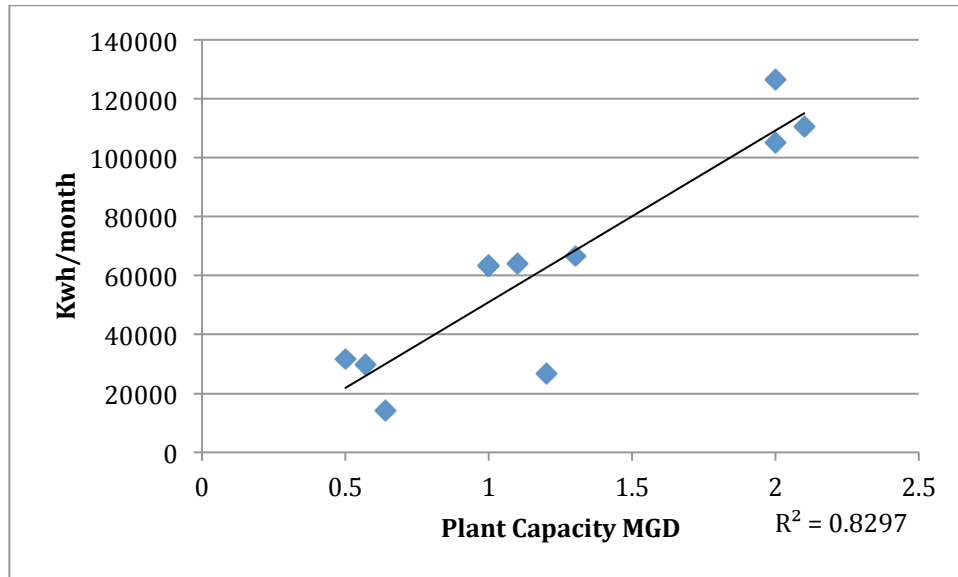


Figure 15: Power Consumption Trend Based on Plant Capacity

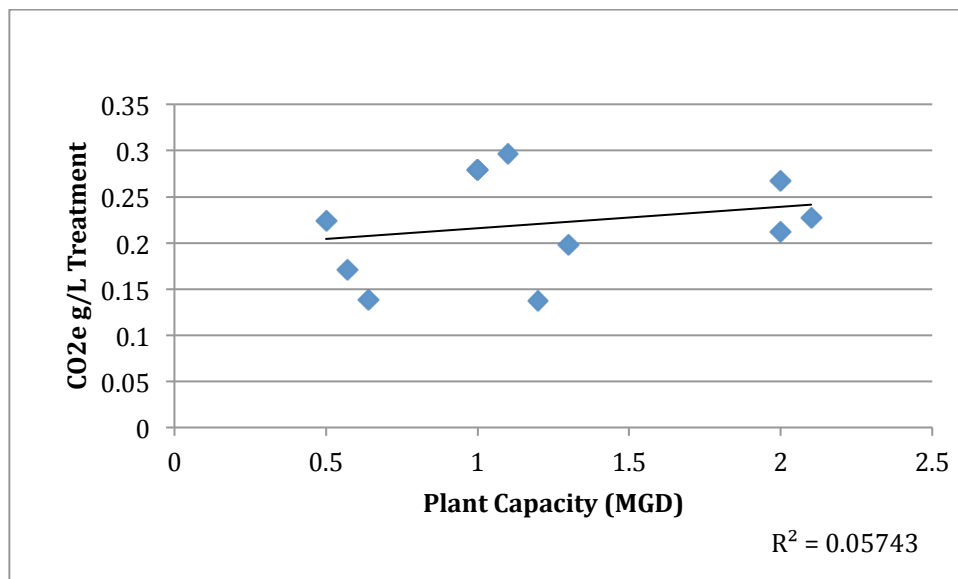


Figure 16: GHG Trend Based on Plant Capacity

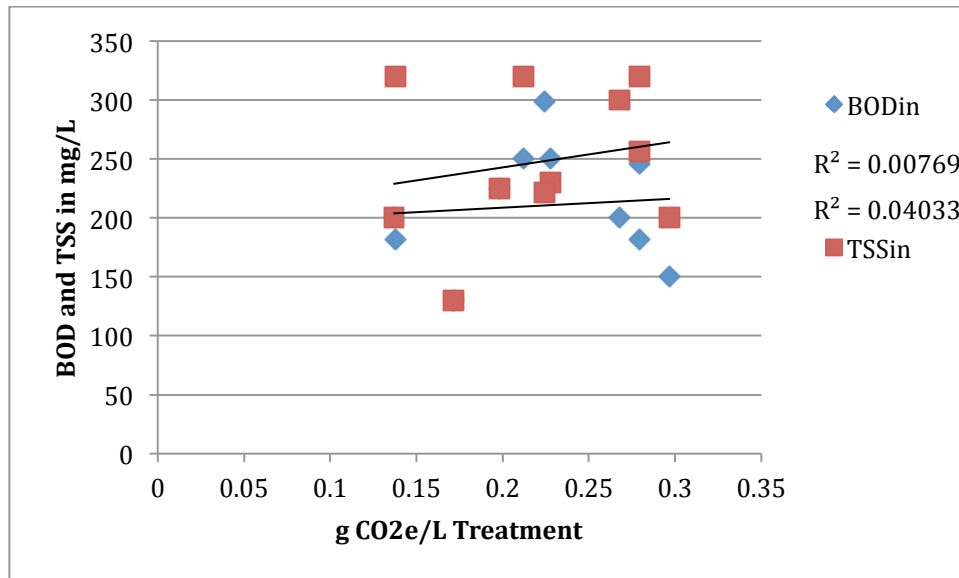


Figure 17: GHG Emissions Based on Influent Concentration

One of the recent trends in wastewater treatment has been towards more concentrated influent. The influents from the WWTPs in this study ranged in concentration from 130-299 mg/L BOD and 130-320 mg/L TSS. In terms of GHG emissions based on the observed BOD and TSS concentrations there was no correlation, which suggests that increased BOD and TSS concentrations alone would not result in higher GHG emissions. This also suggests that the functional unit of mass per liter of wastewater treated is valid even at high wastewater strengths.

CO₂e-WWTP is capable of generating data for more than just the conventional wastewater treatment methods exhibited by the surveyed plants. In order to demonstrate the different possible combinations and the resulting GHG emissions a generalized set of influent data (Table 29) was analyzed with several different plant configurations.

Table 29: Generalized Wastewater Influent

Parameter	Value
Flow	1 MGD
BOD ₅	140 mg/L
TSS	210 mg/L
TKN	32.5 mg/L

Five different combinations of secondary treatment options are shown in Table 30 in order to compare and contrast their GHG emissions. These theoretical plant comparisons were investigated due to the homogeneity of the viable surveyed plants. For the purpose of this comparison none of the theoretical WWTPs below include solids treatment, so it is reasonable when compared to the surveyed plant results that the percentage of N₂O that makes up CO₂e is in the range of 2-4%, whereas if aerobic digestion was present that portion of CO₂e generated from N₂O would be expected to be far greater. Of course these are not all of the possible combinations for treatment; however, it is representative of the variety of combinations possible in CO₂e-WWTP. As is seen in Table 30, the fourth scenario (Primary, Trickling Filter, Secondary Clarifier, and Lagoon) has a much higher CO₂e emission due to treatment alone (0.401 g CO₂e/L) than the other scenarios. The second scenario (Primary, Aeration without Recycle, Secondary Clarifier, and Flotation/Flocculation) has the lowest CO₂e emissions (0.0785 gCO₂e/L) from treatment. The fourth scenario has the highest emissions because it includes two types of biological treatment (trickling filter and lagoon) whereas all of the other scenarios only contain one type of biological treatment. When the CO₂e with the South Carolina power mix was applied to the theoretical WWTPs, the fourth scenario also had the greatest total GHG emissions (0.898 g CO₂e/L); whereas the first scenario (Primary, Trickling Filter, and Secondary Clarifier) had the lowest total overall GHG emissions (0.151 g CO₂e/L).

Table 30: Theoretical GHG Emissions from Standardized Influent

Components	g CO ₂ e /L (Treatment)	g CO ₂ e/L (CH ₄ & CO ₂ e) (Treatment)	g N ₂ O/L (Treatment)	% of CO ₂ e from N ₂ O (Treatment)	SC Power CO ₂ e g/L (Power)	Total g CO ₂ e /L
Primary, Trickling Filter, Secondary Clarifier	0.109	0.106	1.07*10 ⁻⁵	2.75	0.0417	0.151
Primary, Aeration without Recycle, Secondary Clarifier, Flotation/Flocculation	0.0785	0.0756	1.07*10 ⁻⁵	3.67	0.0849	0.193
Primary, RBC, Secondary Clarifier	0.109	0.106	1.07*10 ⁻⁵	2.75	0.112	0.221
Primary, Trickling Filter, Secondary Clarifier, Lagoon	0.410	0.408	1.07*10 ⁻⁵	0.488	0.260	0.898
Primary, RBC, Secondary Clarifier, Activated Carbon	0.109	0.106	1.07*10 ⁻⁵	2.75	0.151	0.260

Table 31 illustrates the large difference in CO₂e emissions from varying the solids treatment but given the same influent wastewater (Table 29) and treatment. The selected treatment system consisted of a primary clarifier, aeration basin with recycle, and a secondary clarifier. Four types of solids treatment were evaluated plus the option of no treatment. When the solids are anaerobically digested or incinerated the percentage of CO₂e emissions from the N₂O contribution is significantly lower than when the solids are aerobically digested or composted. The N₂O emissions appear insignificant when compared with the carbonaceous GHG emissions on a g/L basis, but when their global warming impact is taken into account they become significant. It is also interesting to note that overall the lowest GHG emissions for the system occurred when the solids were anaerobically digested, with composting and incineration as close seconds. Solids

treatment does not dispose of the solids, but typically reduces their volume to make their disposal cost lower. If no solids treatment is performed at the WWTP, those solids would still need to be disposed of, and would have a greater volume than treated solids. Likely the disposal would result in larger CO₂e emissions due to the increased volume that would need to be transported. Typically WWTPs that do not treat their solids landfill them.

GHG emissions from power are an important aspect to consider when comparing and contrasting the overall CO₂e emissions of the different possible solids treatments (Table 31). The treatment that included aerobic digestion had GHG emissions of 0.393 g CO₂e/L, making it the most potent in terms of GHG emissions treatment configuration. When no solids treatment was applied the overall GHG emissions from the theoretical plant were an order of magnitude less at 0.203 g CO₂e/L. This result illustrates that solids treatment can have a large impact on the overall GHG emissions of the WWTP. However, when anaerobic digestion was chosen as the solids treatment the overall GHG emissions were only 0.267 g CO₂e/L. This illustrates that the overall GHG cost of treating the solids, including power emissions contribution, does not have to be that much larger than if there was no solids treatment.

Table 31: Comparison of Different Solids Treatments

Components	g CO ₂ e /L (Treatment)	g CO ₂ e/L (CH ₄ & CO ₂ e) (Treatment)	g N ₂ O/L (Treatment)	% of CO ₂ e from N ₂ O (Treatment)	SC Power Mix g CO ₂ e/L	g CO ₂ e /L
Anaerobic Digestion	0.189	0.182	2.43*10 ⁻⁵	3.70	0.078	0.267
Aerobic Digestion	0.218	0.196	7.88*10 ⁻⁵	10.1	0.175	0.393
Composting	0.191	0.168	7.88*10 ⁻⁵	10.1	0.066	0.369
Incineration	0.274	0.271	1.07*10 ⁻⁵	1.09	0.069	0.372
No Solids	0.137	0.134	1.07*10 ⁻⁵	2.19	0.066	0.203

This study did not include GHG emissions for the transportation of the solids to their end of life whether it is a landfill, land application, or something else. It is possible that the replacement value of the nitrogen that would be utilized for traditional fertilizer could negate the GHG emissions caused by transportation of solids when they are used for agriculture land application. Also, if transportation was modeled per volume of solids that would be transported along with the distance that they must be transported it would equalize the measurements in terms of total GHG emissions to account for the greater volume of untreated solids. Solids that have not been treated generated less GHG emissions according to CO₂e-WWTP but due to the greater volume would create a larger amount of GHG emissions through transportation.

3.5 System Optimization

GHG emissions have in this project been estimated for existing treatment systems. The real utility of CO₂e-WWTP is the possibility of using this tool to build a better wastewater treatment system. It is also important to consider the different power sources to understand how they impact the design for the minimization of GHG emissions. It is true that more often than not the power sources available are not something that the engineer can control.

A generalized wastewater influent was used for the optimization process (Table 32) (Metcalf and Eddy, 2003). The goal for the optimization is to minimize the GHG emissions while still treating the wastewater to an acceptable level. A conventional and simplified WWTP will be examined (Figure 18). The aeration basin is the only unit process that contributes GHG emissions from both power usage and the actual treatment process. The

other processes contribute emissions just from their power requirements. Therefore, the aeration basin will be optimized for both aspects while the others will be simply modeled in terms of their power use. It is important to note that the amount of power used by the primary and secondary clarifiers is assumed to be constant per volume of water treated.

Table 32: Generalized WWTP Influent

Parameter	Quantity
Flow	1 MGD
BOD ₅	140 mg/L
Total Suspended Solids (TSS)	210 mg/L
Nitrogen (N)	40 mg/L
Phosphorus (P)	7 mg/L

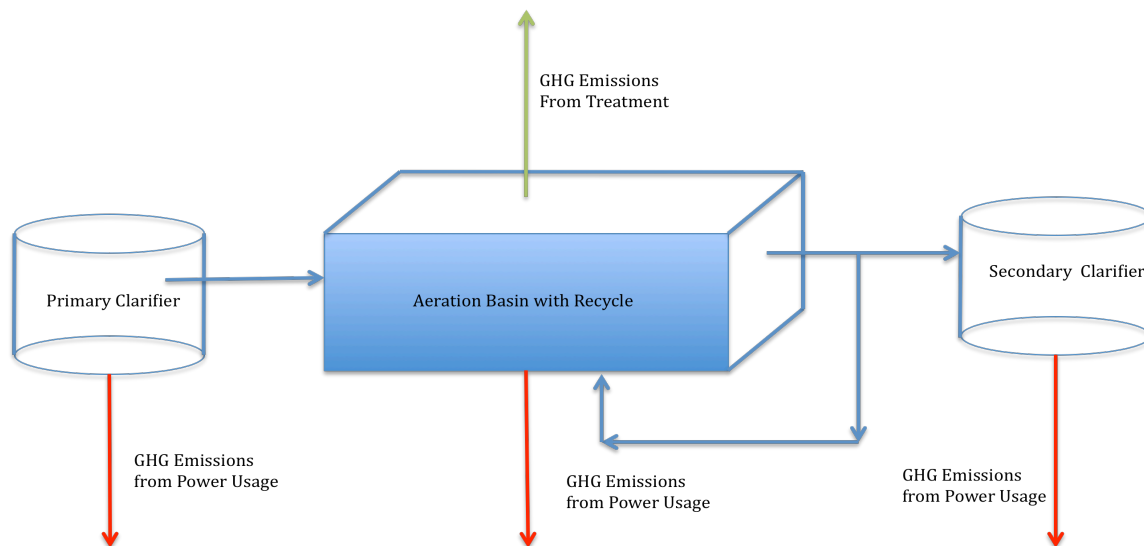


Figure 18: Expected GHG Emission Sources

When the generalized influent (Table 32) was modeled in CO₂e-WWTP (using a conventional plant scenario) the GHG emissions were 0.138 g CO₂e per liter with 1.312×10^5

g N₂O per liter coming from nitrogen, and the theoretical project power usage was 18,446.4 kW per month.

3.5.1 Systems Parameters

The influent first traveled through a primary clarifier with the characteristics shown in Table 32. As was stated before, the primary clarifier was not being optimized, however, the concentrations of interest changes as the influent was passed through the primary clarifier before making its way to the aeration basin.

Table 33: Primary Clarifier Optimization

Parameter	Quantity	Source
Detention Time	4 hours	(Metcalf and Eddy, 2003)
BOD removal	40%	(Metcalf and Eddy, 2003)
TSS removal	65%	(Metcalf and Eddy, 2003)
Nitrogen removal	20%	(Environment Canada, 2009)

The result produced an effluent from the primary clarifier: BOD₅= 84 mg/L, TSS=94.5 mg/L (VSS=61.4 mg/L), TKN=32 mg/L. This effluent served as the influent to the aeration basin where the optimization of the treatment process occurred. In order for optimization to occur values that are held constant within the CO₂e-WWTP were allowed to vary within an acceptable range (Table 34). The ranges shown below correspond to best or general wastewater practices as listed by Metcalf and Eddy (2003).

Table 34: Ranges of Decision Variables for Optimization

Variable	Constraint	Source
x_e	$1.88 \cdot 10^{-4} \geq x_e > 0$ g VSS/m ³	Calculated from (Metcalf and Eddy , 2003)
BOD_{out}	$17.24 \geq$ g BOD/m ³	Calculated from Discharge
V	> 0 , m ³	Assuming that there is no space limitation
r_{O_2}	> 0 , g O ₂ /day	Calculated from (Metcalf and Eddy , 2003)
HRT	4-8 hours	(Metcalf and Eddy , 2003)
SRT	3-15 d	(Metcalf and Eddy , 2003)

Other parameters were held constant, as they were not the decision variables in this case (Table 35). These parameters were largely the same as those applied by Monteith et al. (2005) and utilized in CO₂e-WWTP for other exercises.

Table 35: Aeration Basin Optimization Parameters

Parameter	Value	Source
Aerobic reactor volume (V)	m ³	Decision variable
Influent wastewater average daily flow (Q_i)	3,785.41 m ³	(Metcalf and Eddy , 2003)
Cell-yield coefficient (Y)	0.68 g VSS/g BOD	(Montieth et al., 2005)
Aeration BOD removal rate (r_s)	0.268 g BOD/m ³ *d	Calculated variable using data from (Montieth et al., 2005)
Waste biomass flow (Q_w)	71.9 m ³ /d	(Montieth et al., 2005)
Return biomass concentration (X_r)	$7.5 \cdot 10^6$ mg/m ³	(Montieth et al., 2005)
Aeration Solids Retention Time (SRT)	d	Decision variable
Hydraulic Retention Time (HRT)	hours	Decision variable
Endogenous decay coefficient (k_d)	0.05 /d	(Montieth et al., 2005)
Biomass concentration in aerobic reactor (X)	$1.8 \cdot 10^6$ mg VSS/m ³	(Montieth et al., 2005)
Effluent (X_e)	g VSS/m ³	Decision variable

These parameters were then applied to equations 7-9. It is assumed that the aeration basin is not a significant source of CH₄ production, and that aspect, therefore, can be neglected (Monteith et al., 2005). The assumption was made that the aeration rate of the basin (the amount of oxygen being bubbled in) is equal to the amount of oxygen removed by the BOD removal.

$$r_{O_2} = V * r_s \left(\frac{1}{f} - 1.42Y \right) \quad (37a)$$

The constant $f=0.68$ was utilized from Monteith et al. (2005). The r_s was calculated from an example plant in the study by Monteith et al. (2005) This allowed the r_{O_2} to be calculated based on the volume of the basin. Monteith et al. (2005) concluded that the amount of CO₂ produced in the aeration basin is equal to 1.1 times the amount of oxygen consumed in the aeration basin plus the amount of CO₂ emitted from endogenous decay and respiration. Equations 10-15 allow for the calculation of CO₂ from the aeration basin with recycle. Therefore, calculating r_{O_2} allows not only for an estimation of the aeration rate of the basin, but also for the amount of CO₂ which is produced by the basin. However, this does not account for the contribution from nitrogen. The same method explained earlier was used here to model N₂O emissions (Section 2.12.6).

After the wastewater was treated in the aeration basin it is moved to the secondary clarifier. As was noted before, the secondary clarifier was not optimized, but merely applied to the treatment system. Below are the assumed parameters for the secondary clarifier (Table 36). X_e , which was the concentration of g VSS/m³ was calculated using values from storm run-off. This was done for several reasons. The first reason was the

wide variability of discharge permits that depends on the region where they are issued. And the second was the idea that with tertiary treatment becoming standard in the future, what is released from the plant into a body of water should not be any worse than the run-off entering the body of water. Typical run-off contains on the high end, 101 mg/L of TSS and 10 mg/L of BOD (Metcalf and Eddy , 2003). Assuming that 65% of the TSS remaining in the wastewater is removed in the secondary clarifier and that 65% of the TSS is VSS, then x_e is less than or equal to 187.6 mg VSS/L or 1.88×10^{-4} g VSS/m³.

Table 36: Secondary Clarifier Parameters for Optimization

Parameter	Value
BOD removal	42%
TSS removal	65%

GHG emissions are not only produced by the actual treatment of the wastewater, but also by the power utilized to power the treatment system; therefore, it is important to take into account power needs when minimizing the GHG emissions. The power usage was optimized for the aeration basin, but merely applied for the primary and secondary clarifiers.

For a 1 MGD wastewater treatment plant, the primary clarifier and the secondary clarifier use 15 kwh/d of energy each (WEF, 1997). The aeration rate (r_{O_2}), is then converted into the power used for the process at a rate of 1.5 kg O₂/kwh bubbled in.

Varying the power source used may also impact the optimization of the system. The same CO_{2e} for power sources CO_{2e} that has been utilized throughout this thesis were also used for the optimization (Table 17).

From all of this information that amount of GHG emissions from both wastewater treatment and the power usage to do so, can be accounted for and minimized.

Compiling the equations into a systems format:

$$MinZ = \left[(1.1) * (r_{o2}) * \left(\frac{1}{Q} \right) \right] + \left[1.947 * V * k_d * \left(\frac{1}{Q} \right) \right] + [281 * N_2O] + \left[(r_{o2}) * \left(\frac{1}{Q} \right) * \left(\frac{kWh}{1,500 gO_2} \right) * (E) \right] + \left[(E) * \left(\frac{30kWh}{day} \right) * \left(\frac{1}{Q} \right) \right]$$

(37b)

The equation is made up of several combined terms. The first term on the right hand side of the equation is the CO₂ emitted through growth; the second portion is the CO₂ emitted through respiration and endogenous decay; the third portion of the equation is the N₂O emissions in CO₂e; the fourth portion is the power consumed by aeration and the CO₂e required to generate it; and the fifth portion is the power and emissions from the primary and secondary clarifiers. The results are the emissions in the units of CO₂e g/L.

s.t.

E=emissions factor for each power source

$$SRT = \frac{V * (1800 mg VSS / L)}{(3.71351 * 10^6 L * X_e / d) + (3.1124 * 10^8 mg / d)}$$

$$BOD_{out} \leq 17.24 \frac{g}{m^3}$$

$$VSS_{out} \leq 1.88 * 10^{-4} \frac{g}{m^3}$$

$$3 \leq SRT \leq 15 \text{ days}$$

$$4 \leq \tau \leq 8 \text{ hours}$$

$$BOD_{in} = 84 \frac{g}{m^3}$$

$$VSS_{in} = 61.4 \frac{g}{m^3}$$

$$Q = 3,785.41 \frac{m^3}{day}$$

3.5.2 Optimization Results and Discussion

The power data did not change the effluent or other decision variables when it was varied (Table 37). This suggests that in comparison to the emissions from treatment the power emissions are fairly minor in the optimization. However, the GHG emissions did change for each type of power used (Table 38). Coal was the only power source to be significantly different, falling outside one standard deviation from the mean.

Table 37: Optimized Effluent

Decision Variable	Solutions	Units
xe	0	mg/L
BODout	0	mg/L
V	$6.31 \cdot 10^5$	L
ro2	85.5	g O2/d
HRT	4	hours
SRT	3.65	days

Table 38: Total Minimized GHG Emissions per Liter

Power Source	g CO ₂ e Emissions per Liter
Coal	0.0285
Natural Gas	0.0243
Hydrological	0.0209
Nuclear	0.0209
Wind	0.0210
Solar Photovoltaic	0.0216
Biomass	0.0211
South Carolina	0.0241
United States	0.0253
No power	0.0208

The overall GHG emissions for the unoptimized treatment portion of the plant were 0.138 g CO₂e/L. The optimized system for treatment yields 0.021 g CO₂e/L. This illustrates that the GHG emissions from optimized treatment can be dramatically decreased from those predicted by CO₂e-WWTP for the original system.

When the sensitivity of the system was examined, the binding constraints were found to be the minimum HRT and the minimum Xe. The binding constraint is the parameter that keeps the optimization from being minimized further. In essence it is keeping the overall GHG emissions from being reduced further. It was not possible to relax the parameter for the Xe as it was already set to 0. When the minimum HRT was relaxed from 4 to 2 hours, then the requirement that the SRT must be greater than 3 became binding (Table 39). The SRT was set to be bound as greater than 3 due to the range of acceptable parameters given by Monteith et al. (2005).

Table 39: Solution Set for the Relaxed HRT

Parameter	Value	Units
xe	0	mg/L
BODout	0	mg/L
V	5.19×10^5	L
ro2	70.3	g O ₂ /d
HRT	3.29	hours
SRT	3	days

In comparing the original CO₂e minimization with the relaxed binding constraint minimization the effluent values are found to stay the same. The HRT is lower, being as it was the binding constraint before, and the SRT is lower, being as it is the new binding constraint. The volume of the aeration basin also became smaller, due to the shorter HRT along with the aeration intensity decreasing. The CO₂e emissions changed slightly (0.0311 g CO₂e/L from treatment) when the HRT was relaxed.

As was illustrated by changing the binding constraint, HRT does impact the CO₂e emissions from wastewater treatment. It was also shown, through examining the standard deviation, that all of the power sources are statistically the same in terms of GHG emissions with the exception of coal. CO₂e-WWTP was used to generate GHG emission values from the current design of the WWTP optimized here. Optimization is another tool along with CO₂e-WWTP that allows for the improved design of WWTPs. CO₂e-WWTP is not directly configured to perform optimization modeling, however, by manipulating the constants and the processes selected a more optimum WWTP treatment configuration can be obtained.

Chapter 4

Discussion

Centralized wastewater treatment is an important aspect of life in urban areas, due to the high density of residents; it is necessary for wastewater to be treated not only effectively but efficiently. Smaller plants (2.0 MGD to 0.5MGD) make up 17% of the municipal WWTPs in the United States. Given their prevalence, these plants will have a significant impact on the amount of GHG emissions and energy consumption used for wastewater treatment in the United States. The creation of a user-friendly tool to estimate GHG emissions from smaller scale WWTPs was necessary to obtain a clear picture of what is being emitted. CO₂e-WWTP also provided results that will allow researchers and policy-makers to more accurately evaluate the effect of smaller WWTPs on GHG emissions as well as energy savings. The CO₂e-WWTP tool was designed for estimating GHGs from plants with a treatment capacity of 0.5 MGD to 2.0 MGD. However, CO₂e-WWTP can be used for larger plants, but it may not include all of the options for treatment found in plants of a larger size.

In terms of comparing GHG emissions from WWT to overall GHG emissions for the United States, they make up a very small portion of the total figure (Table 40). As of 2008 “waste-related” activities contributed 2.3% of the total GHG emissions for the United States (EPA, 2010). Some trends that have been observed over the US as a whole for wastewater treatment are that from 1990 to 2008 are CH₄ and N₂O emissions increased by 3.5% and CO₂e emissions increased 34%. The N₂O emissions were generated utilizing the IPCC

protocol discussed earlier in this thesis. That said, the overall contribution from wastewater treatment to United States GHG emissions as a whole is small.

Table 40: US Waste-Sector CO₂e Emissions (Adapted from EPA, 2010)

Gas/Source	(Tg CO ₂ e)	1990	1995	2000	2005	2006	2007	2008
CH₄		173.2	169.6	147.1	151.1	153.1	152.5	152.3
	Landfills	149.3	144.1	120.7	125.6	127.1	126.5	126.3
	Wastewater Treatment	23.5	24.8	25.2	24.3	24.5	24.4	24.3
	Composting	0.3	0.7	1.3	1.6	1.6	1.7	1.7
N₂O		4.0	4.8	5.8	6.5	6.6	6.7	6.8
	Wastewater Treatment	3.7	4.0	4.5	4.7	4.8	4.9	4.9
	Composting	0.4	0.8	1.4	1.7	1.8	1.8	1.8
Total		177.2	174.5	153.0	158.0	159.7	159.3	159.1

Section 3.1 deals with the raw data from plant E, the selected WWTP for the demonstration of the model (Figure 19). Plant E is a suitable representation of the WWTPs in this study because its capacity is 1 MGD which falls within the mid-range of WWTPs modeled in this thesis. The effluent results when projected from CO₂e-WWTP are that some of the TKN would be removed with a significant portion of the TSS and BOD₅ being removed. In order to do this 20.279 CO₂e g/L would be produced by the plant. The secondary treatment would produce 0.164 g CO₂e/L and the remaining portion would come from the solids treatment, producing 0.143 g CO₂e/L. In terms of the contribution of N₂O to GHG emissions from the treatment, 9.74*10⁻⁶ g N₂O/L would be produced from secondary treatment while 1.20*10⁻⁴ g N₂O/L would be produced from the solids treatment. This indicates that in terms of N₂O production and overall GHG emissions, that solids treatment plays a critical role. Expanding on that, 1.67% of the overall CO₂e emissions from secondary treatment can be attributed to N₂O, whereas 23% of the CO₂e emissions for solids treatment. This suggests that nitrogen and N₂O emissions play a fairly

small role in conventional biological treatment in terms of overall GHG emissions, but that they play a much larger role in solids treatment.

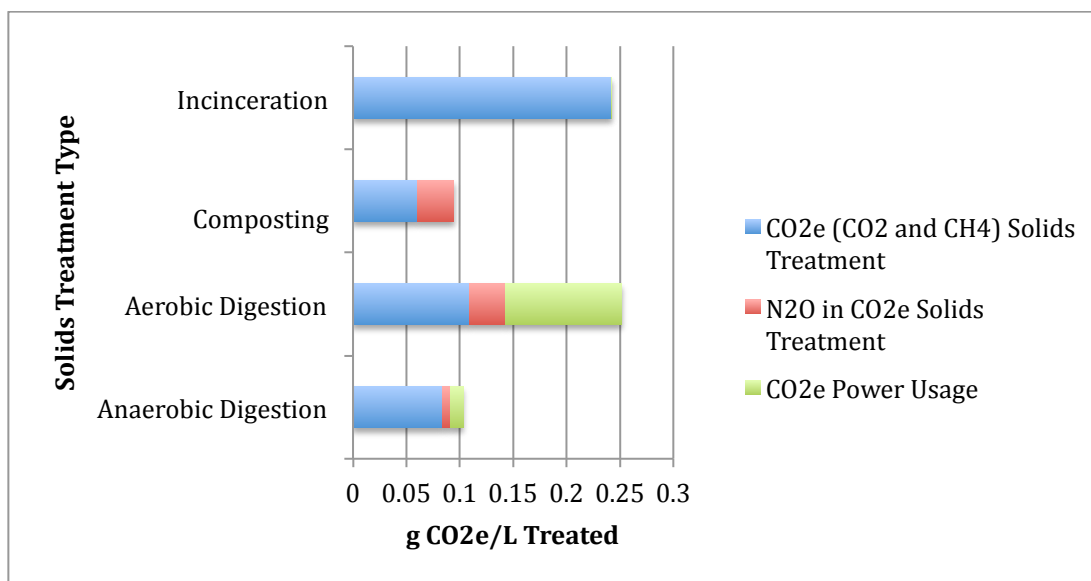


Figure 19: Effects of Solids Treatment on Plant E Overall GHG Emissions

When the different energy sources were applied to plant E a range of 5.38×10^{-3} -0.531 g CO₂e/L was produced which equated to 20,337-2,006,323 CO₂e g/d. The result does not account for other pollution related issues from the fuel sources, such as spent nuclear waste or mercury from coal.

Solids treatment was found to be important to the overall GHG emissions of plant E through the initial modeling. When CO₂e emissions were modeled for just the solids treatment of the solids from plant E, it became apparent that N₂O emissions were more important in some types of treatment than others. CO₂E-WWTP predicts that anaerobic digestion and incineration do not produce significant amounts of N₂O. Aerobic digestion and composting were shown to produce a significant amount of N₂O. This is an important

finding, especially for the majority of the plants surveyed because they process their solids through aerobic digestion.

Plant E was also modeled with possible tertiary treatment options, utilizing both US and South Carolina power mixes. The tertiary options were compared to the current set-up by analyzing the amount of BOD₅ and TKN removed per the amount of CO₂e produced. In terms of BOD removal, the current treatment system without tertiary treatment is most effective at removing BOD in terms of the amount of GHG emissions that are generated. In terms of TKN removal, the lagoon/wetland system was the ideal option, however, the other tertiary treatment options were still effective.

Section 3.2 examined the sensitivity of the assumed parameters in CO₂e-WWTP. With all modeling endeavors it is important to determine how sensitive the assumed parameters are to change, and what impact that will have on the overall result. The complete details of the sensitivity analysis may be found in Appendix F. Certain parameters such as the concentration of VSS were found to have more impact on GHG emissions than other parameters. Some factors, such as HRT, have a relatively small impact, even when they exist within a large possible range. However, other parameters, such as the concentration of VSS that exists within the activated sludge basin, also has a large range of possible values, and affects the GHG emissions, causing a percent change from -20.6 to 121.1%. The process for estimating N₂O emissions was also developed as a part of creating CO₂e-WWTP. This process was fit to the data published by Ahn et al. (2010).

Section 3.4 reported the results of the data analysis of the surveyed WWTPs. Unfortunately, there was not a large variation of plant design exhibited in the surveyed

plants. As a result of this, a generalized result was only determined for two processes: primary treatment with aeration with recycle and a secondary clarifier; and aerobic digestion. On average the CO₂e emissions from conventional primary and secondary treatment was 0.137 g CO₂e/L and produced a range of 0.134-0.138 g CO₂e/L. These values are comparable to those found by Monteith et al. (2005), where CO₂e average values for the primary clarifier was found to be 5.0×10^{-3} g/L and the range for conventional activated sludge treatment as 0.153-0.280 g/L. The N₂O emissions produced by CO₂e-WWTP were an average of 3.73×10^{-6} g N₂O/L and a range of 1.94×10^{-7} - 1.31×10^{-5} g N₂O/L. The overall results from aerobic digestion was an average of 0.106 g CO₂e/L and 8.97×10^{-5} g N₂O/L exhibiting a standard deviation of 0.0414 CO₂e/L and 3.49×10^{-5} g N₂O/L. As these overall results suggest, the average amount of GHG emissions produced by aerobic digestion is within the same order of magnitude as those produced through conventional treatment.

In order to demonstrate the utility and versatility available in CO₂e-WWTP several other different treatment configurations were also evaluated. The results clearly demonstrated that plant configuration can impact the amount of N₂O emitted.

Modeling can also be valuable in optimization of the treatment systems (section 3.5). The GHG emissions from the optimized treatment system were much lower than those generated by CO₂e-WWTP using conventional wastewater treatment parameters.

Aerobic digestion is the more common method of solids treatment in the United States. However, if the GHG emissions produced by it had to be accounted for, that could easily change. In 2009 on the European carbon trading market carbon equivalents cost about \$39 per metric tonne. It is projected, in part due to the economic downturn, that carbon equivalents will cost \$35 per tonne in 2020 (Point Carbon, 2010). The US carbon

trading market is predicted to monitor and eventually charge those users who are producing in excess of 25,000 tons of carbon dioxide yearly (Whelan, 2009). Using the study of GHG emissions based on solids treatment, presented in Table 31, the cost of the CO₂e for each type of solids treatment can be considered. Plant E has a capacity of 1 MGD and assuming 365 days a year of operating time, it processes 365 million gallons.

None of the solids treatment scenarios cause Plant E to have emissions at or in excess of 25,000 tons per year. However, if a WWTP wanted to reduce its CO₂e emissions and sell all of its carbon allowances, the profits could be substantial. As can be seen in Table 44, the overall savings if all the CO₂e credits were sold on the market for each plant could be substantial. Another way to think about it, is if a WWTP was not under the 25,000 ton yearly allowance and had to pay for every gram of CO₂e it produced, then this would be the amount that the plant would have to pay for the CO₂e it produced.

Table 41: Carbon Cost of Treatment

Components	g CO ₂ e /L (Treatment)	g CO ₂ e /L (Power)	g CO ₂ e /L (Total)	Tonnes CO ₂ e per year	US \$ /day	US \$/year
PC, AwR, SC, AnD	0.189	0.078	0.267	97.46	9.35	3,411
PC, AwR, SC, AD	0.218	0.175	0.393	143.45	13.75	5,020
PC, AwR, SC, C	0.191	0.066	0.369	143.45	13.75	5,020
PC, AwR, SC, I	0.274	0.069	0.372	135.78	13.02	4,752
PC, AwR, SC	0.137	0.066	0.203	74.10	7.11	2,593
PC=Primary Clarifier, AwR=Aeration with Recycle, SC=Secondary Clarifier , AnD=Anaerobic Digestion AD=Aerobic Digestion, C=Composting, I=Incineration						

It is also interesting to note that activated carbon and rapid sand filtration are not the most common methods for removing BOD or TKN, but in this set of results were the more effective methods per unit of CO₂e at removal. This result does not take into account

any of the operational costs and other considerations that would be important when deciding whether to install these treatment methods at a WWTP.

The question can also be posed as to whether the 11 plants within South Carolina are a reasonable number from which to draw conclusions. In the study by Ahn et al. (2010) on N₂O emissions from activated sludge processes across the United States the sample size was only twelve plants (Ahn et al., 2010). Also, the Canada-wide study performed by Monteith et al. (2005) used full-scale data from sixteen plants across Canada and then fit model to the ten provinces across Canada to come up with projections of carbonaceous GHG emissions.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

Several conclusions about GHG emissions and wastewater treatment can be drawn from this thesis and modeling experience. A user-friendly model (CO₂e-WWTP) has been created that allows for the estimation of GHG emissions from conventional WWTPs and using a variety of power generation sources. A method of estimating N₂O emissions from WWTP has also been created, which allows the contributions of N₂O emissions to the overall GHG emission to be quantified. One conclusion is that although N₂O generation is not significant in the actual treatment process of conventional wastewater treatment systems it is significant in terms of solids treatment, particularly aerobic digestion treatment. The second conclusion is that, not including N₂O emissions, incineration produces the most GHG emissions of any solids treatment. A third conclusion is that it is important to evaluate the trade-offs between GHG emissions and BOD/TKN removal. The fourth conclusion is that operational costs must be considered. Design must also consider pumping requirements and how they will affect GHG emissions and power use. The fifth conclusion is that commonly the GHG emissions from power are much less than those from the actual treatment process. The South Carolina power mix produces less GHG emissions than the United States power mix.

There were four objectives set at the beginning of this thesis. The first objective was to model GHG emissions from WWTPs given a set amount of information about the influent

and the treatment scenario. This objective was accomplished with data being gathered from 11 WWTPs that fit the established criteria for the study. The second objective was to compare actual and theoretical energy usage from the WWTPs. This objective was not accomplished due to a lack of available data. When the surveys were returned the majority of the WWTPs did not supply that information or gave information that was incorrect by several orders of magnitude. This forced all of the estimations about GHG emissions from energy usage to be done using the theoretical WWTP data that neglects pumping between system processes. The third objective was to compare power usage with GHG production. GHG emissions from power usage, when a South Carolina power mix is applied, are approximately equal to those from conventional wastewater treatment without solids treatment. This suggests that power usage is equally important in terms of reducing overall GHG emissions to treatment changes. The fourth objective was to model a process change such as tertiary treatment on the conventional WWTPs surveyed. This was completed and the results suggested that although tertiary treatment is an important way to clean the effluent further that it does so at a greater cost in grams of CO₂e emitted per g of TKN or BOD removed than conventional wastewater treatment. It is still, however, an important tool when the effluent quality is of high concern.

5.2 Recommendations

There is a great need for more research in the area of GHG emissions from WWTPs. Currently, there is a lack of in-situ studies done at WWTPs in terms of GHG emissions. This not only pertains to those about nitrogen and its transformations, but also carbon. In terms of better understanding what end products will be produced, more research is needed on the populations of microbes that inhabit the aeration basins and other biological treatment

aspects of wastewater treatment. More research into these areas would allow for better models to predict GHG emissions from wastewater treatment.

Beyond just wastewater treatment, transportation and end of life of solids should also be included to gain a more comprehensive view of GHG emissions. Currently, it is difficult to create a model that encompasses both the treatment and power emissions along with transportation and end of life for the solids emissions; more research into this area will allow for better modeling and predictions. This future research into the GHG emissions from solids treatment would help to give a larger and more equitable view of GHG emissions especially those from plants who choose not to treat their solids onsite.

Appendices

Appendix A-Survey

Plant Name:_____

Plant Location:_____

Flow (MGD):_____

If flow is not available, approximate population served:_____

Monthly power consumption:_____

Influent Components:

BOD (mg/L):_____

TSS (mg/L):_____

Phosphorus (mg/L):_____

Nitrogen(TKN) (mg/L):_____

Is Primary Treatment Present:_____

Select Primary Treatment that applies (and add comments as appropriate):

☐ Primary clarifier:_____

☐ Other treatment:_____

Is Secondary Treatment Present:_____

Select Secondary Treatment that applies and (add comments as appropriate):

☐ Aeration tank with sludge recycling:_____

☐ Aeration basin without sludge recycling:_____

☐ Trickling filter:_____

☐ Biological filter:_____

☐ Membrane Bio-reactor:_____

☐ Other:_____

☐ Secondary Clarifier:_____

☐ Floatation:_____

Is Tertiary Treatment Present:_____

Select Tertiary Treatment that applies, and identify treatment objective (e.g., Nitrogen Removal).

Add other comments as appropriate.

☐ Sand filtration:_____

☐ Activated carbon filtration:_____

☐ Lagoon:_____

☐ Constructed wetlands:_____

☐ Disinfection:_____

☐ Other:_____

☐ Nitrogen removal:_____

☐ Phosphorus removal:_____

☐ Odor removal:_____

Is the sludge treated:_____

Select sludge treatment that applies (and add comments as appropriate):

☐ Anaerobic digestion:_____

☐ Aerobic digestion:_____

☐ Composting:_____

☐ Incineration:_____

☐ Other:_____

Is the Effluent treated before discharge: If so how?

Appendix B-Secondary Treatment Equations

The secondary treatment example shown in the text is for an aeration basin with recycle. In this section parameters and equations for the other types of secondary treatment in CO₂e-WWTP will be given.

The first alternate type of secondary treatment considered is an aeration basin without recycle. The same equations, 7-9, still apply; however, the parameters shown in Table 2 may be slightly different. All of the parameters are the same with the exception of the recycle flow (Q_w) and the wasting concentration (X_r), which in this case is zero due to the fact that wasting/recycle will not be occurring. Equations 10-16, for the estimation of carbonaceous GHG emissions are the same.

The second alternate type of secondary treatment is a trickling filter. The same equations, 7-9, will still apply; however, some of the parameters in Table 2 are different. The solids retention time (SRT) is 20 days for a trickling filter. Equations 10-16, for the estimation of carbonaceous GHG emissions are the same.

The third alternate type of secondary treatment is a RBC. The same equations, 7-9, still apply; however, some of the parameters in Table 2 are different. As with the trickling filter the SRT is 20 days for the RBC. Equations 10-16, for the estimation of carbonaceous GHG emissions are the same.

The fourth type of secondary treatment is flotation/flocculation. The following parameters for flotation/flocculation are shown in the equations below and come from a study done by Odegaard (2000). It is important to note that the data used to formulate

these parameters are from flocculation. From literature review it is assumed that there will be no direct GHG emissions from flotation/flocculation.

$$flotationoutflowbod = 0.136 * influentflotationbod \quad (b1)$$

$$flotationoutflowvss = 0.099 * influentflotationvss \quad (b2)$$

The fifth type of secondary treatment is a secondary clarifier. It was modeled using the following equations (Metcalf and Eddy , 2003).

$$secondaryclarifierBODout = 0.58 * secondaryclarifierBODin \quad (b3)$$

$$secondaryclarifierVSSout = 0.37 * secondaryclarifierVSSin \quad (b4)$$

Although there are other types of secondary treatment available, they are not considered conventional, and therefore are not included in CO₂e-WWTP.

Appendix C-Tertiary Treatment Equations

The example given for tertiary treatment is a lagoon; it is important to note that lagoon and wetland treatment are the same process. In this section the parameters and equations for the other types of tertiary treatment in CO₂e-WWTP are given.

The first alternate type of tertiary treatment is sand filtration. It is assumed that there are no direct GHG emissions from rapid sand filtration. The parameters used in CO₂e-WWTP are from a study by Hamoda et al. (2004).

$$\text{sandfilterBODout} = 0.8 * \text{sandfilterBOBDin} \quad (\text{c1})$$

$$\text{sandfilterVSSout} = 0.56 * \text{sandfilterVSSin} \quad (\text{c2})$$

The second alternate type of tertiary treatment is activated carbon. It is assumed that there are no direct GHG emissions from activated carbon (Metcalf and Eddy, 2003).

$$q_{\text{BOD}} = (((5 * 10^4) * (\text{secondaryBODout})) - (3.5 * 10^5)) / (2.75 * 10^7) \quad (\text{c3})$$

$$\text{flowhourly} = \text{Adjinfluent} * (1 / 24) \quad (\text{c4})$$

$$\text{activatedcarbonBODout} = (((\text{flowhourly}) * (\text{secondaryBODout}) * (0.16)) - ((2.75 * 10^7) * q_{\text{BOD}})) / (\text{flowhourly} * 0.16) \quad (\text{c5})$$

The VSS concentration is expected to stay the same as before it entered the activated carbon.

Disinfection is assumed to be ultra violet (UV), and will exhibit only a power demand. Although many other types of novel tertiary treatment exist, such as nutrient removal, they are not included in the CO₂e-WWTP model.

Appendix D-ANOVA Analysis

Figure D1: ANOVA Results

Analysis of Variance (One-Way)							
<i>Descriptive Statistics</i>							
Groups	Sample size	Sum	Mean	Variance			
Biomass	7	0.1344	0.0192	0.0026			
Coal (Co2e g/L)	7	3.33863	0.47695	1.60707			
Hydrological	7	0.03386	0.00484	0.00017			
Natural Gas	7	1.54027	0.22004	0.34205			
Nuclear	7	0.03766	0.00538	0.0002			
SC	7	1.42864	0.20409	0.29427			
Solar Photovoltaic	7	0.33687	0.04812	0.01636			
US	7	1.97842	0.28263	0.56433			
Wind	7	0.10192	0.01456	0.0015			
Total	63		0.14176	0.0252			
<i>ANOVA</i>							
Source of Variation	d.f.	SS	MS	F	p-level	F crit	Omega Sqr.
Between Groups	8	1.53666	0.19208	400.4122	0.E+0	2.54035	0.98066
Within Groups	54	0.0259	0.00048				
Total	62	1.56257					
Hartley Fmax	9,722.36245	Degrees Of Freedom	9	6			
Cochran C	0.56816	Degrees Of Freedom	9	6			
Bartlett Chi-square	145.52414	Degrees Of Freedom	8	p-level	0.E+0		

Figure D2: Fisher LSD

Fisher LSD							
Group vs Group (Contrast)	Difference	Test Statistics	p-level	Accepted?			
Biomass vs Coal (Co2e g/L)	-0.45775	39.09926	0.E+0	accepted			
Biomass vs Hydrological	0.01436	1.22686	0.22501	rejected			
Biomass vs Natural Gas	-0.20084	17.15494	0.E+0	accepted			
Biomass vs Nuclear	0.01382	1.18048	0.2428	rejected			
Biomass vs SC	-0.18489	15.7928	0.E+0	accepted			
Biomass vs Solar Photovoltaic	-0.02892	2.47058	0.01656	rejected			
Biomass vs US	-0.26343	22.50142	0.E+0	accepted			
Biomass vs Wind	0.00464	0.3963	0.69339	rejected			
Coal (Co2e g/L) vs Hydrological	0.47211	40.32612	0.E+0	accepted			
Coal (Co2e g/L) vs Natural Gas	0.25691	21.94432	0.E+0	accepted			
Coal (Co2e g/L) vs Nuclear	0.47157	40.27975	0.E+0	accepted			
Coal (Co2e g/L) vs SC	0.27286	23.30646	0.E+0	accepted			
Coal (Co2e g/L) vs Solar Photovoltaic	0.42882	36.62868	0.E+0	accepted			
Coal (Co2e g/L) vs US	0.19432	16.59785	0.E+0	accepted			
Coal (Co2e g/L) vs Wind	0.46239	39.49557	0.E+0	accepted			
Hydrological vs Natural Gas	-0.2152	18.3818	0.E+0	accepted			
Hydrological vs Nuclear	-0.00054	0.04638	0.96318	rejected			
Hydrological vs SC	-0.19925	17.01966	0.E+0	accepted			
Hydrological vs Solar Photovoltaic	-0.04329	3.69744	0.0005	accepted			
Hydrological vs US	-0.27779	23.72828	0.E+0	accepted			
Hydrological vs Wind	-0.00972	0.83055	0.40975	rejected			
Natural Gas vs Nuclear	0.21466	18.33542	0.E+0	accepted			
Natural Gas vs SC	0.01595	1.36213	0.17861	rejected			
Natural Gas vs Solar Photovoltaic	0.17191	14.68436	0.E+0	accepted			
Natural Gas vs US	-0.06259	5.34648	0.	accepted			
Natural Gas vs Wind	0.20548	17.55124	0.E+0	accepted			
Nuclear vs SC	-0.19871	16.97329	0.E+0	accepted			
Nuclear vs Solar Photovoltaic	-0.04274	3.65106	0.00058	accepted			
Nuclear vs US	-0.27725	23.6819	0.E+0	accepted			
Nuclear vs Wind	-0.00918	0.78418	0.43624	rejected			
SC vs Solar Photovoltaic	0.15597	13.32222	0.E+0	accepted			
SC vs US	-0.07854	6.70861	0.	accepted			
SC vs Wind	0.18953	16.18911	0.E+0	accepted			
Solar Photovoltaic vs US	-0.23451	20.03084	0.E+0	accepted			
Solar Photovoltaic vs Wind	0.03356	2.86689	0.00583	accepted			
US vs Wind	0.26807	22.89772	0.E+0	accepted			

Appendix E-Solids Treatment Equations

The example equations given for solids treatment are from anaerobic digestion. In this section parameters and equations for the other types of solids treatment in CO₂e-WWTP are given.

The first type of alternate solids treatment is for aerobic digestion.

$$vs\ deg\ aer = 0.45 * solidsprocessed \quad (e1)$$

$$co2aero = vs\ deg\ aer * 1.9469 \quad (e2)$$

Equation e1 assumes that 45% of the solids are removed through aerobic digestion.

Equation e2 assumes that 1.9469 grams of CO₂e are produced per grams of solids aerobically digested (Monteith et al., 2005).

The second alternate type of solids treatment is composting.

$$vs\ deg\ comp = 0.25 * solidstobeprocessed \quad (e3)$$

$$co2comp = 1.9469 * vs\ deg\ comp \quad (e4)$$

Equation e3 uses the parameter from Metcalf and Eddy (2003) that 25% of the solids are removed by volume. Equation e4 uses the parameter of 1.9469 gram of CO₂e per gram of solids processed. According to Metcalf and Eddy (2003) the main products of composting are CO₂ and water. Although there are some nitrogenous emissions, they are discussed in the solids portion of the paper, Sections 2.10 and 2.11.

The third type of alternate solids treatment is incineration.

$$co2incin = 1.9469 * solidstobeprocessed \quad (e5)$$

Equation d5 gives the amount of CO₂ in grams per grams of solids processed.

Appendix F-Sensitivity Analysis

In modeling, a sensitivity analysis allows for the examination and determination of which parameters have the greatest impact on the outcome of the system. The portion of CO₂e-WWTP for the emissions of CO₂ and CH₄ come largely from the study by Monteith et al (2005). Many of the parameters and values used in that study gave a value and then also a range of possible acceptable values for that term. In analyzing the sensitivity, those ranges of values were used. The nitrogenous emissions portion of CO₂e-WWTP was discussed in Section 2.12. However, in order to fit with the analytical observations on a survey of WWTPs done by Ahn et al. (2010) only a certain percentage of the possible nitrogen that was available to go through nitrification and denitrification was assumed. Different percentages will be explored here.

The sensitivity analysis was performed using Plant E, which was also the plant used as the example for the CO₂e-WWTP as a whole and for the optimization portion of the report. Plant E was chosen due to the fact that its capacity is within the target range of this model and it has no tertiary treatment other than disinfection and a phosphorus filter. However, seeing as phosphorus is not considered in CO₂e-WWTP it simply presents an additional energy demand.

Table F1 and Figure F1 illustrate the large amount of percentage change for N₂O emissions based on assuming that a different percentage of the NH₃ is available for nitrification/dentrification. When the sensitivity was investigated at both ends of the range (90-115%) of the NH₃ being available, the overall change in CO₂e was less than one percent. This suggests that it is not a very sensitive parameter.

Table F1: Sensitivity of NH₃ Available for CO₂e Emissions

Percentage of available NH ₃ entering nitrification/denitrification	CO ₂ e grams/Liter	Percent change
90%	2.79*10 ⁻¹	-0.0980
95%	2.79*10 ⁻¹	-0.0490
100%	0.279	0
105%	0.279	0.0490
110%	0.279	0.0980
115%	0.280	0.147

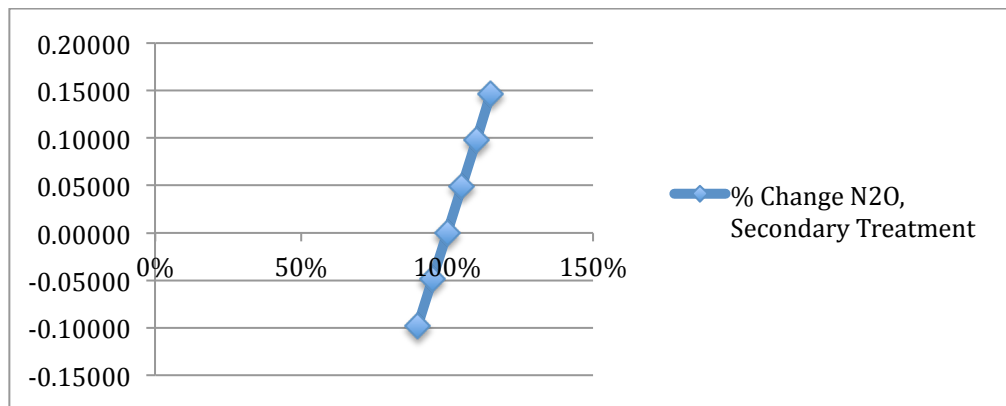


Figure F1: Percent Change in N₂O Emissions

Tables F2 and F3 along with Figures F2 and F3 illustrate the sensitivity of CAS and lagoon/wetland emissions in terms of HRT. The figures also show the percent change in terms of just that single component of the system, and the impact that it has on the system's CO₂e emissions as a whole. By varying the HRT within the accepted parameters for the CAS system, the percent change of the CO₂e emissions for that treatment process varied from -49.8% to +33.2%, this represents a rather large range for the process. When the effect of varying the HRT for the CAS was compared to the overall treatment system for the entire treatment system, the percent change of CO₂e emissions ranged from -36.2% to

+24.1%. When the HRT was varied for the lagoon/wetland treatment system, there was a significant percent change in CO₂e emissions for that portion of the treatment system, ranging from -43.2% to 108 %. However, when the change in CO₂e emissions was compared to the treatment system as a whole, the percent change seemed less significant, varying from -21.6% to +54.0%.

Table F2: HRT Impact on Conventional Activated Sludge Systems (CAS)

HRT (CAS) hours	CO ₂ e emissions (g/L) from 2ndary	% Change	CO ₂ e emissions (g/L) from Total System	% Change
3	0.0685	-49.8	0.178	-36.2
4	0.0911	-33.2	0.212	-24.1
5	0.114	-16.6	0.246	-12.1
6	0.136	0	0.279	0
7	0.159	16.6	0.313	12.1
8	0.182	33.2	0.347	24.1

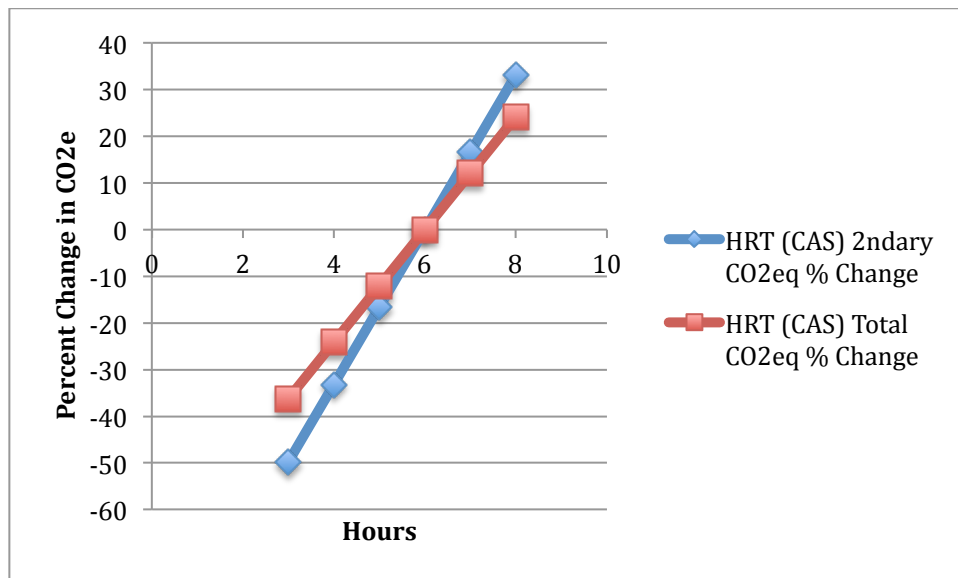


Figure F2: Sensitivity of HRT in CAS

Table F3: Sensitivity of HRT in Lagoon/Wetland

HRT (Lagoon) hours	CO ₂ e emissions (g/L) from 3rdary	% Change	CO ₂ e emissions (g/L) from Total System	% Change
72	0.159	-43.2	0.438	-21.6
80	0.179	-36.0	0.458	-18.0
90	0.204	-27.0	0.483	-13.5
100	0.229	-18.0	0.508	-9.00
120	0.279	0	0.559	0
130	0.304	9.00	0.584	4.50
140	0.330	18.0	0.609	9.00
150	0.355	27.0	0.634	13.5
160	0.380	36.0	0.659	18.0
170	0.405	45.0	0.684	22.5
180	0.430	54.0	0.709	27.0
190	0.455	63.0	0.734	31.5
200	0.480	72.0	0.760	36.0
210	0.506	81.0	0.785	40.5
220	0.531	90.0	0.810	45.0
230	0.556	99.0	0.835	49.5
240	0.581	108	0.860	54.0

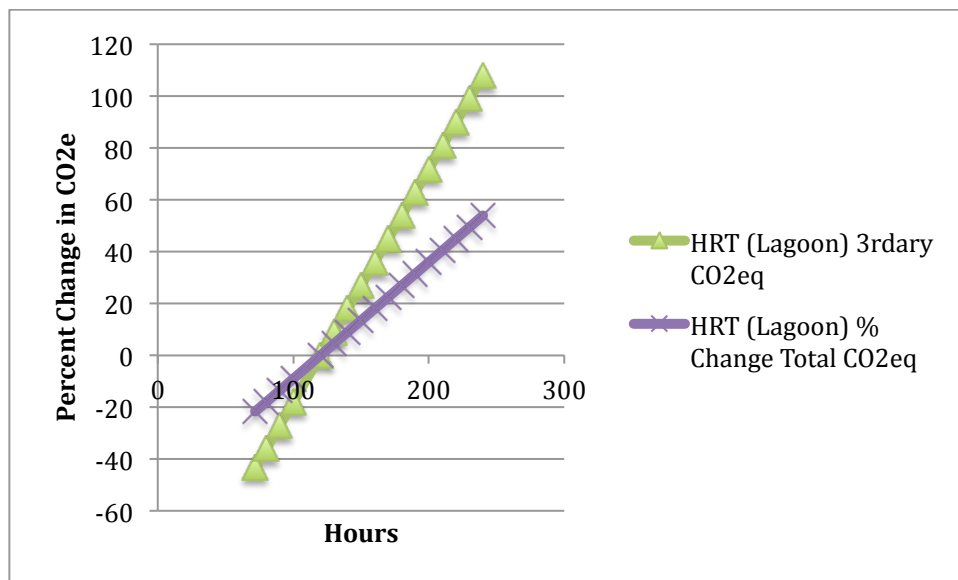


Figure F3: Sensitivity of HRT in Lagoon/Wetland

As can be seen in Tables F4 through F6 and Figure F4, SRT can have a large impact on the GHG emissions generated by the system. It is important to note, however, that some of the SRTs considered existed in a very large range of acceptable values, such as those for wetland/lagoons. When the SRT was varied within the acceptable parameters for the CAS system, the percentage change of system in terms of CO₂e ranged from -35.9% to 35.9% and for the overall system from -0.334% to 0.334%. When the SRT for the wetland/lagoon system was allowed to vary within the acceptable parameter range, the percent change in CO₂e for the system ranged from -39.0% to 39.0% and for the overall system from -19.5% to 19.5%. When the SRT for the RBC was allowed to vary within the acceptable parameter range, the percent change in CO₂e emissions was -7.65% to 0% and for the overall system -6.69% to 0%.

Table F4: Sensitivity of SRT in a CAS System

SRT (CAS) days	CO ₂ e emissions (g/L) from 2ndary	% Change	CO ₂ e emissions (g/L) from Total System	% Change
3	0.185	35.9	0.373	0.334
4	0.155	13.5	0.314	0.125
5	0.136	0	0.279	0
6	0.124	-8.99	0.256	-0.0836
7	0.115	-15.4	0.239	-0.143
8	0.109	-20.2	0.227	-0.188
9	0.104	-24.0	0.217	-0.223
10	0.0996	-27.0	0.209	-0.251
11	0.0962	-29.4	0.203	-0.273
12	0.0935	-31.5	0.198	-0.292
13	0.0911	-33.2	0.193	-0.309
14	0.0891	-34.7	0.189	-0.322
15	0.0873	-35.9	0.186	-0.334

Table F5: Sensitivity of SRT on Lagoon/Wetland

SRT (Lagoon) days	CO ₂ e emissions (g/L) from 3rdary	% Change	CO ₂ e emissions (g/L) from Total System	% Change
3	0.388	39.0	0.667	19.5
4	0.320	14.6	0.599	7.31
5	0.279	0	0.559	0
6	0.252	-9.75	0.531	-4.88
7	0.233	-16.7	0.512	-8.36
8	0.218	-21.9	0.497	-11.0
9	0.207	-26.0	0.486	-13.0
10	0.198	-29.2	0.477	-14.6
11	0.190	-31.9	0.469	-16.0
12	0.184	-34.1	0.463	-17.1
13	0.179	-36.0	0.458	-18.0
14	0.174	-37.6	0.454	-18.8
15	0.170	-39.0	0.450	-19.5
3	0.388	39.0	0.667	19.5

Table F6: Sensitivity of SRT on RBC

SRT (RBC) days	CO ₂ e emissions (g/L) from 2ndary	% Change	CO ₂ e emissions (g/L) from Total System	% Change
20	0.0812	0	0.174	0
21	0.0803	-1.08	0.173	-0.956
22	0.0795	-2.06	0.171	-1.83
23	0.0788	-2.95	0.170	-2.62
24	0.0781	-3.77	0.168	-3.35
25	0.0775	-4.53	0.167	-4.02
26	0.0770	-5.22	0.166	-4.63
27	0.0764	-5.87	0.165	-5.21
28	0.0760	-6.47	0.164	-5.74
29	0.0755	-7.02	0.163	-6.23
30	0.0751	-7.54	0.163	-6.69

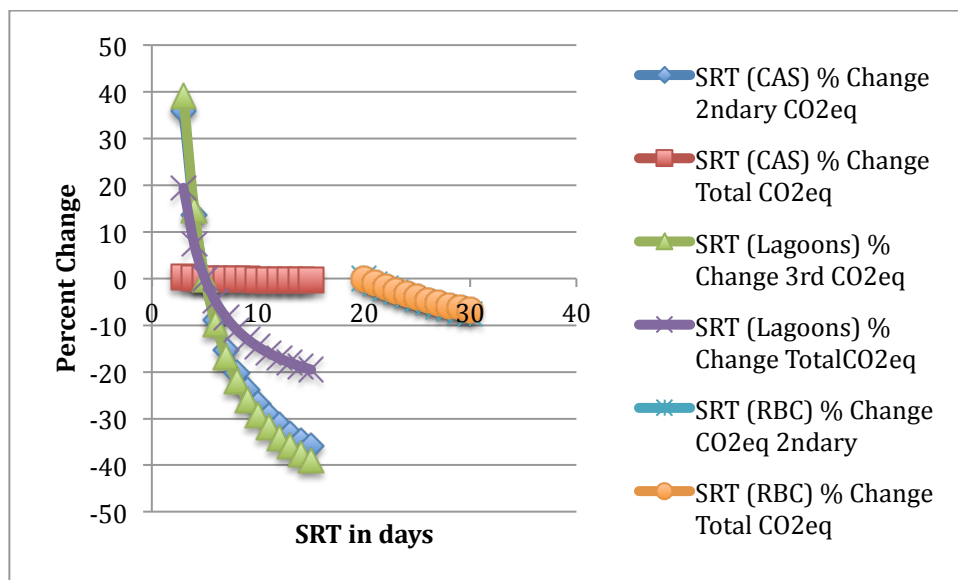


Figure F4: Sensitivity of SRT on GHG Emissions

As can be seen in Tables F7 through F9 and Figures F5 and F6, X (which is the amount of VSS in mg/L) already contained in the system can have an effect on the amount of GHG emissions produced from the system. When the VSS concentration was allowed to vary within the range of acceptable parameters for the CAS system, the percent change of the CO₂e emissions was -24.0% to 141% and for the overall system -22.3% to 131.0%. When the VSS concentration was allowed to vary within the acceptable parameter range for RBC, the percent change in CO₂e for the system was -44.1% to 259%, and for the overall system was -24.8% to 146%. Some buffering by the system can be seen when the VSS concentration was allowed to vary in the acceptable range for the lagoon/wetland system. The percent change of CO₂e emissions for the system ranged from -54.0% to 32.4%, however, for the overall system the range was much smaller at -27.0% to 16.2%.

Table F7: Sensitivity of X on CAS

X (CAS) mg VSS/L	CO ₂ e emissions (g/L) from 2ndary	% Change	CO ₂ e emissions (g/L) from Total System	% Change
1000	0.104	-24.0	0.217	-22.3
1100	0.108	-21.0	0.225	-19.5
1200	0.112	-18.0	0.233	-16.7
1300	0.116	-15.0	0.240	-13.9
1400	0.120	-12.0	0.248	-11.1
1500	0.124	-8.99	0.256	-8.36
1600	0.128	-5.99	0.264	-5.57
1700	0.132	-3.00	0.271	-2.79
1800	0.136	0	0.279	0
1900	0.140	3.00	0.287	2.79
2000	0.145	5.99	0.295	5.57
2100	0.149	8.99	0.303	8.36
2200	0.153	12.0	0.310	11.1
2300	0.157	15.0	0.318	14.0
2400	0.161	18.0	0.326	16.7
2500	0.165	21.0	0.334	19.5
3000	0.185	35.9	0.373	33.4
3500	0.206	50.9	0.411	47.3
4000	0.226	65.9	0.450	61.3
4500	0.247	80.9	0.489	75.2
5000	0.267	95.9	0.528	89.1
5500	0.297	118	0.567	103
6000	0.308	126	0.606	117
6500	0.328	141	0.645	131

Table F8: Sensitivity of X on RBC

X (RBC) mg VSS/L	CO ₂ e emissions (g/L) from 2ndary	% Change	CO ₂ e emissions (g/L) from Total System	% Change
1000	0.0454	-44.1	0.131	-24.8
1100	0.0499	-38.6	0.136	-21.7
1200	0.0544	-33.1	0.142	-18.6
1300	0.0588	-27.6	0.147	-15.5
1400	0.0633	-22.0	0.153	-12.4
1500	0.06778	-16.5	0.158	-9.30
1600	0.0723	-11.0	0.163	-6.20
1700	0.0767	-5.51	0.169	-3.10
1800	0.0812	0	0.174	0
1900	0.0857	5.51	0.180	3.10
2000	0.0902	11.0	0.185	6.20
2100	0.0946	16.5	0.190	9.30
2200	0.0991	22.0	0.196	12.4
2300	0.104	27.6	0.201	15.5
2400	0.108	33.1	0.207	18.6
2500	0.113	38.6	0.212	21.7
3000	0.135	66.1	0.239	37.2
3500	0.157	93.7	0.266	52.7
4000	0.180	121	0.293	68.2
4500	0.202	149	0.320	83.7
5000	0.224	176	0.347	99.2
5500	0.247	204	0.374	115
6000	0.270	231	0.401	130
6500	0.292	259	0.428	146

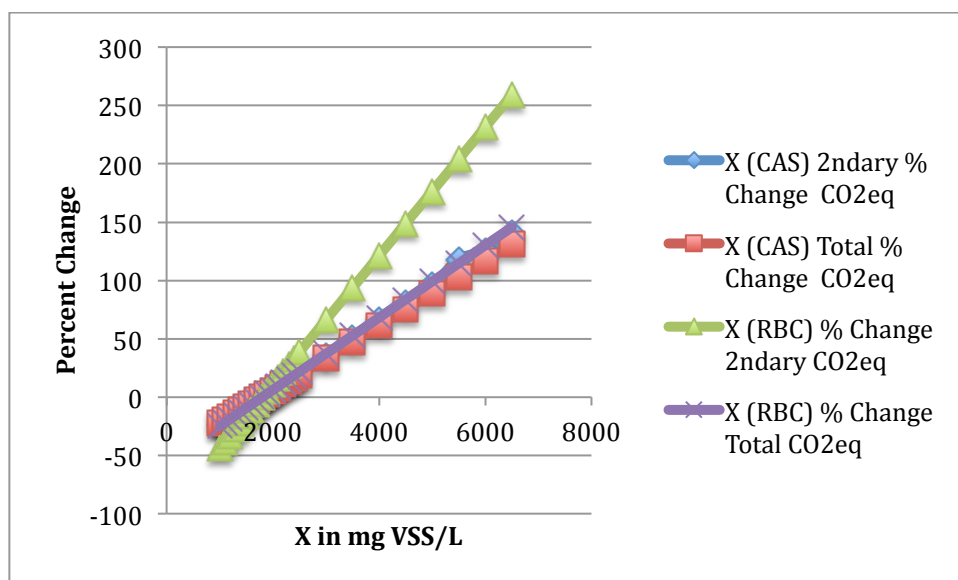


Figure F5: Sensitivity of X for CAS and RBC GHG Emissions

Table F9: Sensitivity of X for Lagoon/Wetland GHG Emissions

X (Lagoon) mg VSS/L	CO ₂ e emissions (g/L) from 3rdary	% Change	CO ₂ e emissions (g/L) from Total System	% Change
100	0.129	-54.0	0.408	-27.0
110	0.144	-48.6	0.428	-24.3
120	0.159	-43.2	0.438	-21.6
130	0.174	-37.8	0.453	-18.9
140	0.189	-32.4	0.468	-16.2
150	0.204	-27.0	0.483	-13.5
160	0.219	-21.6	0.498	-10.8
170	0.234	-16.2	0.513	-8.10
180	0.249	-10.8	0.528	-5.40
190	0.264	-5.40	0.543	-2.70
200	0.279	0	0.559	0
210	0.294	5.40	0.574	2.70
220	0.310	10.8	0.589	5.40
230	0.325	16.2	0.604	8.10
240	0.340	21.6	0.619	10.8
250	0.355	27.0	0.634	13.5
260	0.370	32.4	0.649	16.2

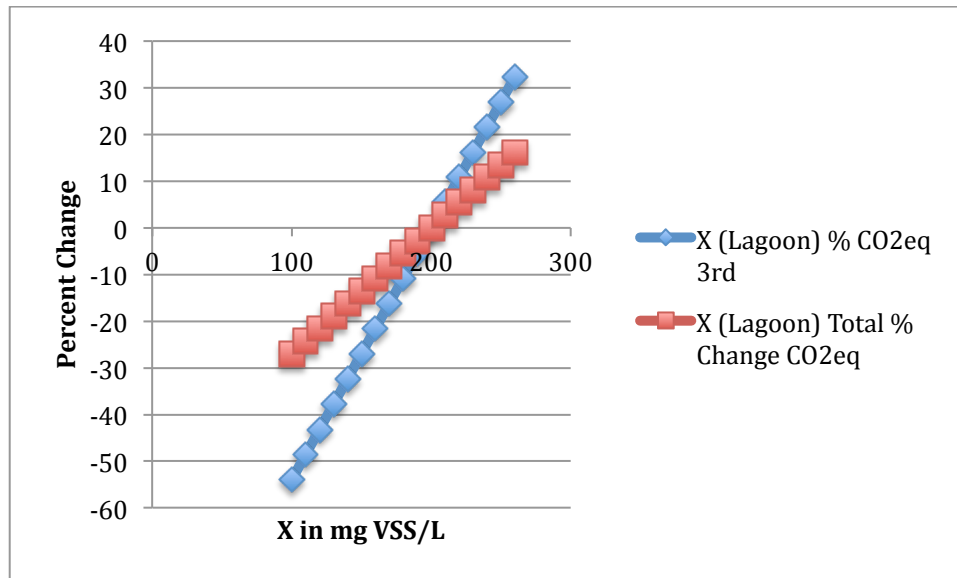


Figure F6: Sensitivity of X for Lagoon/Wetland GHG Emissions

As can be seen in Tables F10 and F11 along with Figure F7, the endogenous decay coefficient (k_d) does impact that amount of GHG emissions produced from the system. When compared to the overall system's amount of GHG emissions, however, the impact appears to be fairly small. When the k_d was allowed to vary within the acceptable range for the CAS system the CO₂e emissions varied from -12.4% to 6.74%, but the overall system emissions only varied from -6.06% to 3.29%. The same type of overall system impact can be seen in the wetland/lagoon system for k_d . When the k_d was allowed to vary in the acceptable parameter range the percent change in CO₂e emissions for the system ranged from -45.5% to 24.7% and for the overall system from -22.8 to 12.4%.

Table F10: Sensitivity of kd on GHG Emission from CAS

kd (CAS) mg d ⁻¹	CO ₂ e emissions (g/L) from 2ndary	% Change	CO ₂ e emissions (g/L) from Total System	% Change
0.004	0.119	-12.4	0.262	-6.06
0.005	0.120	-12.1	0.263	-5.92
0.015	0.123	-9.44	0.266	-4.61
0.03	0.129	-5.39	0.272	-2.63
0.045	0.135	-1.35	0.277	-0.658
0.05	0.136	0	0.279	0
0.06	0.140	2.70	0.283	1.32
0.075	0.146	6.74	0.288	3.29

Table F11: Sensitivity of kd on Lagoon/Wetland GHG Emissions

kd (Lagoon) mg d ⁻¹	CO ₂ e emissions (g/L) from 3rdary	% Change	CO ₂ e emissions (g/L) from Total System	% Change
0.004	0.152	-45.5	0.431	-22.8
0.005	0.155	-44.5	0.434	-22.3
0.015	0.183	-34.6	0.462	-17.3
0.03	0.224	-19.8	0.503	-9.90
0.045	0.266	-4.95	0.545	-2.47
0.05	0.279	0	0.559	0
0.06	0.307	9.894	0.586	4.95
0.075	0.348	24.7	0.628	12.4

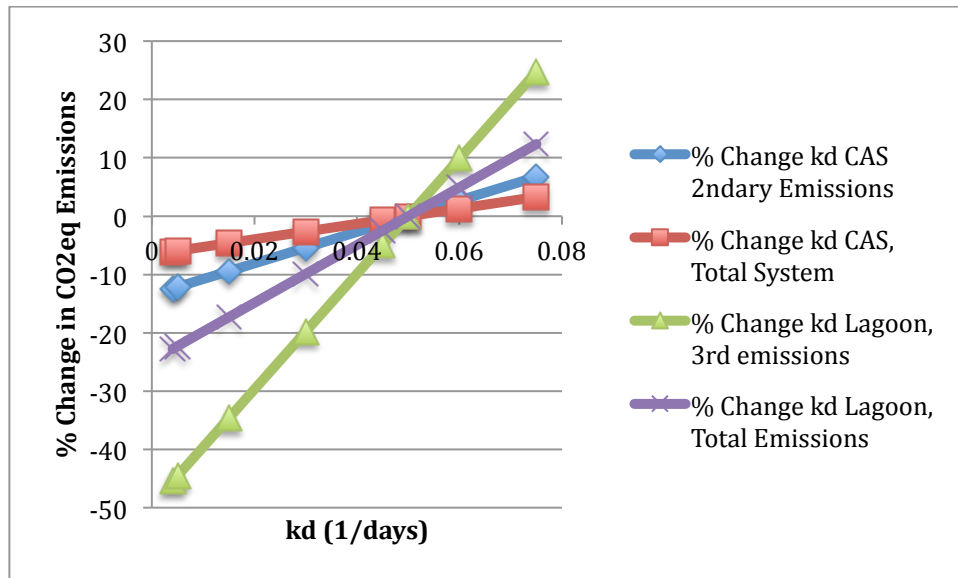


Figure F7: Sensitivity of kd on GHG Emissions from CAS and Lagoon/Wetland

Tables F12 through F14 and Figures F8 through F10, illustrate the sensitivity of GHG emissions based on assumptions made about the solids destruction and treatment. When the percentage of solids reduction in the aerobic digester was allowed to vary within the acceptable range, the percent change in CO₂e emissions for the system ranged from -25.4% to 16.9% and for the overall system from -13.0% to 8.66%. When the destruction rate for the anaerobic digester was allowed to vary within the acceptable range the percent change in CO₂e emissions ranged from -15.4% to 22.6% for the system and for the overall system from -6.21% to 9.10%. The composition of the biogas in the anaerobic digester was also allowed to vary within the acceptable range, and the percent change found in CO₂e emissions was found to be -31.2% to 40.6%.

Table F12: Sensitivity of GHG Emissions from Percent Aerobic Solids Reduction

Aerobic Digester Solids Reduction (%)	CO ₂ e emissions (g/L) from Solids Treatment	% Change	CO ₂ e emissions (g/L) from Total System	% Change
30	0.107	-25.4	0.243	-13.0
35	0.119	-16.9	0.255	-8.66
40	0.131	-8.47	0.267	-4.33
45	0.143	0	0.279	0
50	0.155	8.46	0.291	4.33
55	0.167	16.9	0.303	8.66

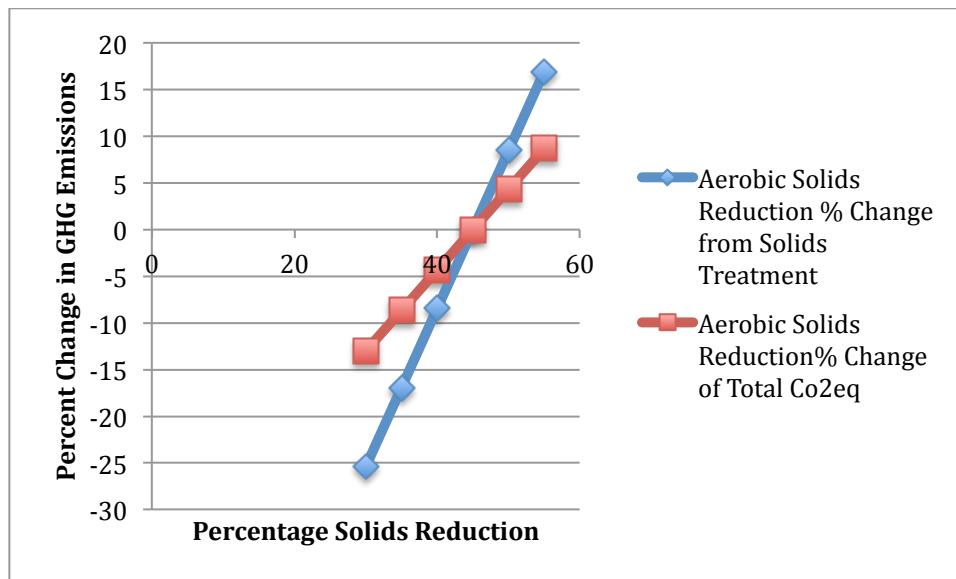


Figure F8: Sensitivity of Solids Reduction on GHG Emissions from Aerobic Digestion

Table F13: Sensitivity of GHG Production Based on Destruction Rate

Anaerobic Digester Biogas Production (m3/kg vss destroyed)	CO ₂ e emissions (g/L) from Solids Treatment	% Change	CO ₂ e emissions (g/L) from Total System	% Change
0.75	0.0776	-15.4	0.214	-6.21
0.8	0.0823	-10.3	0.219	-4.14
0.85	0.0870	-5.14	0.223	-2.07
0.9	0.0917	0	0.228	0
0.95	0.0964	5.14	0.233	2.07
1	0.101	10.3	0.237	4.14
1.05	0.106	15.4	0.242	6.21
1.1	0.111	20.6	0.247	8.27
1.12	0.112	22.6	0.249	9.10

Table F14: Sensitivity of GHG Emissions from Composition of Biogas Produced

Anaerobic digester biogas volume CH ₄ (%)	Anaerobic digester biogas volume CO ₂ (%)	CO ₂ e emissions (g/L) from Solids Treatment	% Change	CO ₂ e emissions (g/L) from Total System
55	42	0.118	28.9	11.6
60	37	0.105	14.5	5.82
65	32	0.0917	0	0
70	27	0.0784	-14.5	-5.82
75	22	0.06517136	-28.9	-11.6
52	45	0.12619846	37.6	15.1

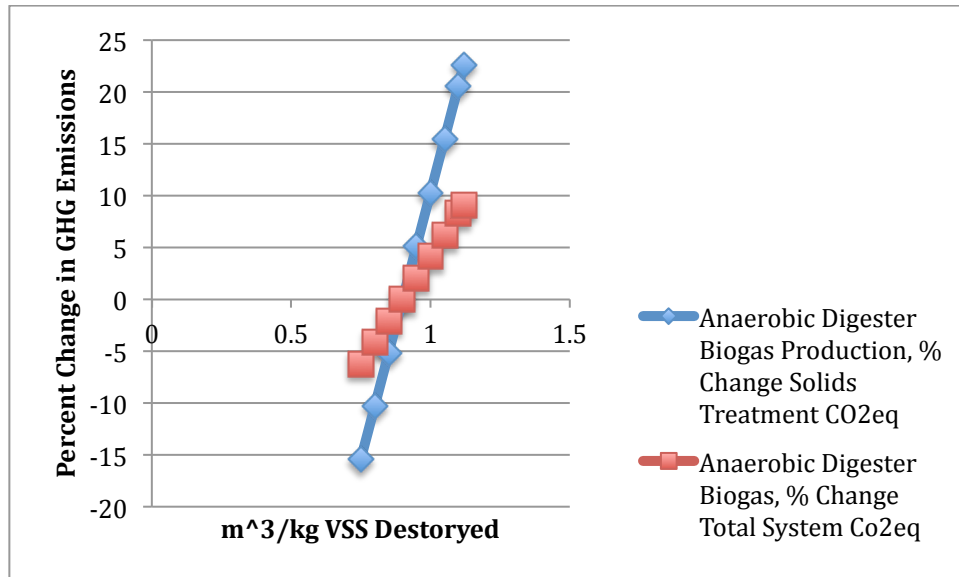


Figure F9: Sensitivity of GHG Emissions to Anaerobic Destruction Rate

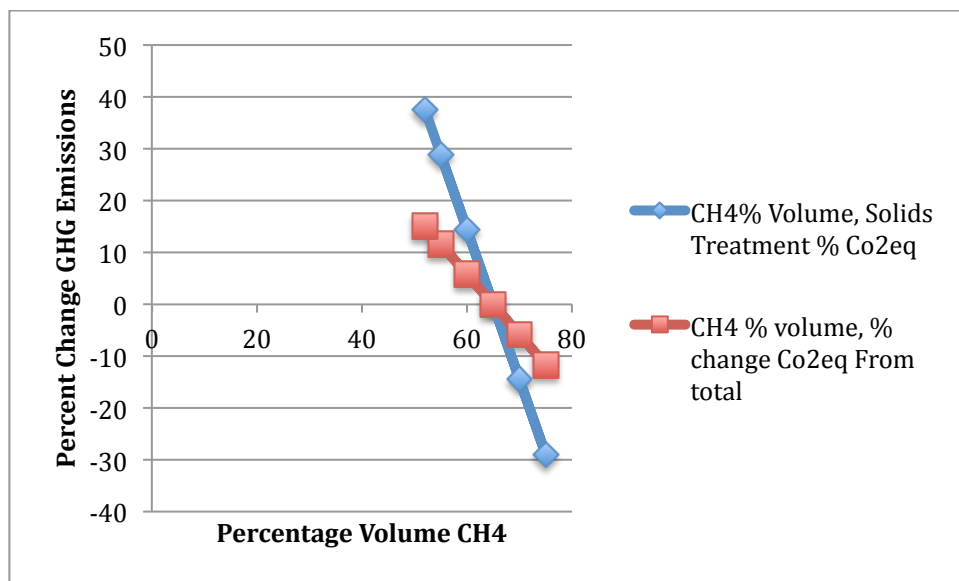


Figure F10: GHG Emission Sensitivity to Biogas Composition

In the sensitivity analysis it was found that although some of the parameters have a larger acceptable range that in itself does not guarantee that it will cause a greater percentage change of CO₂e emissions in the system than a parameter with a smaller range.

References

- Ahn, J. H., Kim, S., Park, H. P., Rahm, B., Pagilla, K., and Chandran, K. (2010). N₂O emissions from activated sludge processes, 2008-2009: Results of a national monitoring survey in the United States. *Environmental Science and Technology*, 44 4505-4511.
- Bahgat, M., Dewedar, A., and Zayed, A. (1998). Sand-filters used for wastewater treatment: buildup and distribution of microorganisms. *Water Resources*, 33 (8), 1949-1955.
- Barford, C. C., Montoya, J. P., Altabet, M. A., and Mitchel, R. (1999). Steady-state nitrogen isotope effects of N₂ and N₂O production in *Paracoccus denitrificans*. *Applied and Environmental Microbiology*, 65 (3), 989-994.
- Brodrick, S. J., Cullen, P., and Maher, W. (1987). Denitrification in a natural wetland receiving secondary treated effluent. *Water Resources*, 22 (4), 431-439.
- Cakir, F., and Stenstrom, M. (2005). Greenhouse gas production: A comparison between aerobic and anaerobic wastewater treatment technology. *Water Research*, 39, 4197-4203.
- Central Intelligence Agency. (2010 January). *Urbanization*. Retrieved 2010 11-January from The world Factbook: <https://www.cia.gov/library/publications/the-world-factbook/fields/2212.html>
- Colliver, B., and Stephenson, T. (2000). Production of nitrogen oxide and dinitrogen oxide by autotrophic nitrifiers. *Biotechnology Advances*, 18, 219-232.
- Cooke, W. B., and Hirsch, A. (1958). Continuous sampling of trickling filter populations: II. Populations. *Sewage and Industrial Wastes*, 30 (2), 138-156.
- Czepiel, P., Crill, P., and Harris, R. (1995). Nitrous oxide emissions from municipal wastewater treatment. *Environmental Science and Technology*, 29, 2352-2356.
- De Nevers, N. (2000). *Air Pollution Control Engineering*. Boston : McGraw-Hill.
- El-Fadel, M., and Massoud, M. (2001). Methane emissions from wastewater management. *Environmental Pollution*, 114, 177-185.
- Environmental Protection Agency. (n.d.). *Climate Change*. Retrieved 2010 25-May from EPA: <http://www.epa.gov/climatechange/emissions/downloads06/07ES.pdf>
- Environmental Defense Fund. (2009 9-March). *Environmental Defense Fund*. Retrieved 2010 22-June from Innovation Exchange: <http://innovation.edf.org/page.cfm?tagID=37020>
- Environmental Protection Agency . (2000 September). *Trickling Filter Nitrification*. Retrieved 2010 1-May from Wastewater Technology Fact Sheet .
- Environmental Protection Agency. (2008 18-January). *2004 Clean Water Needs Survey US EPA*. Retrieved 2009 30-September from Watershed assesment, tracking results system: http://iaspub.epa.gov/water10/query_tool.before_simple

Environmental Protection Agency. (2009a 2-December). *Greenhouse Gas Equivalencies Calculator*. Retrieved 2009 12-December from Green energy:
<http://www.epa.gov/RDEE/energy-resources/calculator.html>

Environmental Protection Agency. (2005). *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2005*. US EPA.

Environmental Protection Agency. (2010 5-January). *Greenhouse Gas Equivalencies Calculator*. Retrieved 2010 26-February from Clean Energy:
<http://www.epa.gov/RDEE/energy-resources/calculator.html#results>

Energy Information Administration. (2010). *Independent Statistics and Analysis Electric Power Monthly April 2010*. US Energy Information Administration.

Environmental Protection Organization . (2010). *Inventory of U.S. greenhouse gas emissions and sinks: 1990 – 2008*. Washington, D.C.: US EPA.

Environment Canada. (2009 12-June). *NPRI Guidance Manual for the Wastewater Sector*. Retrieved 2010 26-April from Environment Canada: www.ec.gc.ca

Gupta, A., and Gupta, S. (1999). Simultaneous carbon and nitrogen removal in a mixed culture aerobic RBC biofilm . *Water Resources* , 33 (2), 555-561.

Hamoda, M., Al-Ghusian, I., and Al-Jasem, D. (2004). Application of granular media filtration in wastewater reclamation and reuse. *Journal of Environmental Health and Science* , A39 (2), 385-395.

Heiss, B., Frunzke, K., and Zumft, W. G. (1989). Formation of the N-N Bond from nitric oxide by a membrane- bound cytochrome bc complex of nitrate-respiring (denitrifying) *Pseudomonas stutzeri*. *Journal of Bacteriology* , 171 (6), 3288-3297.

Heylen, K. (2007). *Study of the genetic basis of denitrification in pure culture denitrifiers isolated from activated sludge and soil*. Gent, Belgium: University of Ghent.

Hiatt, C. W. (2006). Activated sludge modeling for elevated nitrogen concentrations. *Doctoral Dissertation* . Clemson, SC, USA: Clemson University .

Hittlebaugh, J. A., and Miller, R. D. (1981). Operational problems with rotating biological contactors. *Water Environment Federation* , 53 (8), 1283-1293.

Houillon, G., and Jolliet, O. (2005). Life cycle assesment of processes for the treatment of wastewater urban sludge: Energy and global warming analysis. *Journal of Cleaner Production* , 13, 287-299.

Huail, T., Shah, S. D., Miller, J. W., Younglove, T., Chernich, D. J., and Ayala, A. (2006). Analysis of heavy-duty diesel truck activity and emissions data. *Atmospheric Environment* , 40, 2333-2344.

Huang, T., and Tseng, S. (2001). Nitrate reduction by *Citrobacter diversus* under aerobic environment. *Applied Microbiology and Biotechnology* , 90-94.

Inamori, R., Gui, P., Dass, P., Matsumura, M., Xu, K.-Q., Kindo, T., Ebie, Y., and Inamori, Y. (2007). Investigating CH₄ and N₂O emissions from eco-engineering wastewater treatment processes using constructed wetland microcosms. *Process Biochemistry*, 42, 363-373.

Jeppsson, U., Alex, J., Pons, M.N., Spangers, H., and Vanrolleghen, P.A. (2002). Status and future trend of ICA wastewater treatment - a European perspective. *Water Science and Technology*, 45 (4-5), 485-494.

Kakutani, T., Beppu, T., and Arima, K. (1980). Regulation of nitrite reductase in the denitrifying bacterium *Alcaligenes faecalis* S-6. *Agricultural Biological Chemistry*, 45 (1), 23-28.

Kampschreur, M. J., Temmink, H., Kleerebezen, R., Jetten, M. S.M., and van Loosdrecht, M.C.M., (2009). Nitrous oxide emission during wastewater treatment. *Water Research*, 43, 4093-4103.

Keller, J., and Hartley, K. (2003). Greenhouse gas production in wastewater treatment: process selection is the major factor. *Water Science and Technology*, 47 (12), 43-48.

Kester, R. A., DeBoer, W., and Laanbroek, H. (1997). Production of NO and N₂O by pure cultures of nitrifying and denitrifying bacteria during changes in aeration. *Applied and Environmental Microbiology*, 63 (10), 3872-3877.

Koch, F. H. (2000). Hydropower-Internalized Costs and Externalized Benefits. *International Energy Agency (IEA)-Implementing Agreement for Hydropower Technologies and Programs*. Retrieved 2010 9-September from Nuclear Energy Institute:
<http://www.nei.org/resourcesandstats/documentlibrary/protectingtheenvironment/graphicsandcharts/lifecycleemissions/>

Koch, G., Egli, K., Van de Meer, J., and Siegrist, H. (2000). Mathematical modeling of autotrophic denitrification in a nitrifying biofilm of a rotating biological contactor. *Water Science and Technology*, 41 (4), 191-198.

Kong, H., Kimochi, Y. M., and Inamori, Y. (2002). Study of the characteristics of CH₄ and N₂O emission and methods of controlling their emission in the soil-trench wastewater treatment process. *The Science of the Total Environment*, 290, 59-67.

Lettinga, G. (1995). Anaerobic digestion and wastewater treatment systems. *Antonie van Leeuwenhoek*, 67, 3-28.

Levernz, H., and Tchobanoglous, G. (2007). Identification of research needs for effective low cost wastewater treatment technologies. *Water Environment Federation*.

Malhotra, S., Lee, G., and Rohlich, G. (1964). Nutrient removal from secondary effluent by alum flocculation and lime precipitation. *International Journal of Air and Water Pollution*, 8, 487-500.

Mata-Alvarez, J., Mace, S., and Llabres, P. (2000). Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Biosource Technology* , 74, 3-16.

(2010b). *Materials Characterization Paper In Support of the Proposed Rulemaking: Identification of Nonhazardous Secondary Materials That Are Solid Waste Wastewater Treatment Sludge*. Retrived 2010 9-September from Environmental Protection Agency: <http://www.epa.gov/waste/nonhaz/define/pdfs/wwt-sludge.pdf>

Maynard, H., Ouki, S., and Williams, S. (1998). Tertiary lagoons: A review or removal mechanisms and performance. *Water Resources* , 33 (1), 1-13.

Meier, P. J. (2002). *Life-cycle assesment of electricity generation systems and applications for climate change policy analysis*. Madison, WI, USA: Univesrity of Wisconsin, Madision.

Metcalf and Eddy . (2003). *Wastewater Engineering Treatment and Resue*. New York : McGraw Hil.

Microbiologyprocedure.com. (n.d.). *Activated Sludge Process*. Retrieved 2010 19-October from Microbiologyprocedure.com: <http://www.microbiologyprocedure.com/waste-water-microbiologyII/activated-sludge-process.html>

Middlebrooks, E., and Middlebrooks, C. R. (1981). Energy requirements for small wastewater treatment systems. *Water Pollution Control Federation* , 53 (7), 1172-1197.

Monteith, H., Kalogo, Y., and Louzeiro, N. (2007). Achieving stringent effluent limts takes a lot of energy! *Water Environment Federation* , 4343-4356.

Monteith, H., Sahley, H., MacLean, H., and Bagely, D. (2005). A rational procedure for estimation of greenhouse-gas emissions from wastewater treatment plants. *Water Environment Research* , 77 (4), 390-403.

Monteny, G., Groenestein, C., and Hilhorst, M. (2001). Interactions and coupling between emissions of methane and nitrous oxide from animal husbandry. *Nutrient Cycling in Agroecosystems* , 60, 123-132.

Najjar, V. A., and Allen, M. (1953). Formation of nitrogen, nitrous oxide, and nitric oxide by extracts of dentirifying bacteria . *Journal of Biological Chemistry*, 206, 209-214

National Oceanic And Atmospheric Administration. (2009 28-August). *Nitrous Oxide Now Top Ozone- depleting Emission*. Retrieved 2010 24-May from Science Daily : <http://www.sciencedaily.com /releases/2009/08/090827141344.htm>

Nichols, D. S. (1983). Capacity of natural wetlands to remove nutrients from wastewater . *Water Environment Federation* , 55 (5), 495-505.

Odegaard, H. (2000). The use of dissolved air floatation in municipal wastewater treatment . *Norwegian University of Science and Technology* .

Ott, R., and Longnecker, M. (2001). *An Introduction to Statistical Methods and Data Analysis* (5 ed.). Pacific Grove , California , USA: Duxbruy Publishing .

Peigne, J., and Girardin, P. (2004). Environmental impacts of farm-scale composting practices. *Air, Water, and Soil Pollution* , 153, 45-68.

Point Carbon . (2010). Carbon Market Insights 2010. *Carbon 2010 Return of the sovereign*. Amsterdam .

Pynaert, K., Smets, B. F., Wyffels, S., Beheydt, D., Siciliano, S. D., and Verstraete, W. (2003). Characterization of an autotrophic nitrogen-removing biofilm from a highly loaded lab-scale rotating biological contactor. *Applied and Environmental Microbiology* , 69 (6), 3626-3635.

Rashad and Hammad. (1999). Nuclear power and the environment: Comparative assessment of environmental and health impacts of electricity-generating systems. *Applied Energy* , 65, 211-229.

Rashad, S., and Hammad, F. (2000). Nuclear power and the environment: comparative assessment of environmental and health impact of electricity generating systems. *Applied Energy* , 65, 211-229.

Reignders, L., and Huijbregts, M. (2008). Palm oil and the emission of carbon-based greenhouse gases. *Journal of Cleaner Production* , 16, 477-482.

Rosso, D., and Stenstrom, M. K. (2008). The carbon-sequestration potential of municipal waste treatment. *Chemosphere* , 70, 1468-1475.

Schalutman, M. (2010 19-October). Personal communication .

Scheehle, E., and Dorn, M. (2003). Improvements to the U.S. wastewater methane and nitrous oxide emissions estimates. Retrieved 2010 9-September from Environmental Protection Agency: <http://www.epa.gov/ttnchie1/conference/ei12/green/scheehle.pdf>

Schramm, A. (2003). In situ analysis of structure and activity of the nitrifying community in biofilms, aggregates, and sediments. *Geomicrobiology Journal* , 20, 313-333.

Shahabadi, M. Y., and Haghighat, F. (2009). Impact of process design on greenhouse gas (GHG) generation by wastewater treatment plants. *Water Research* , 43, 2679-2687.

Shiskowski, D. M., and Mavinic, D. S. (2006). The influence of nitrite and pH (nitrous acid) on aerobic-phase, autotrophic N₂O generation in a wastewater treatment bioreactor. *Journal of Environmental Engineering and Science* , 5, 273-283.

Spieles, D. J., and Mitsch, W. J. (1998). The effects of season and hydrologic and chemical loading on nitrate retention in constructed wetlands: a comparison of low- and high-nutrient riverine systems. *Ecological Engineering* , 14, 77-91.

- St. John, R. T., & Hollocher, T. C. (1977). Nitrogen 15 tracer studies on the pathway of denitrification in *Pseudomonas aeruginosa*. *The Journal of Biological Chemistry* , 252 (1), 212-218.
- Suh, Y.-J., and Rousseaux, P. (2001). An LCA of alternative wastewater sludge scenarios. *Resources, Conservation, and Recycling* , 35 (191-200) .
- Suwaj, Y., Suzuki, T., Toyohara, H., Yamagishii, T., and Urushigawa, Y. (1992). Single stage, single sludge nitrogen removal by an activated sludge process with cross-flow filtration. *Water Resources* , 26 (9), 1149-1157.
- Svoboda, K., D., B., and Martinec, J. (2006). Nitrous oxide emissions from waste incineration. *Institute of chemistry* , 60 (1), 78-90.
- Tal, Y., Watts, J. E., Schreier, S. B., Sowers, K. R., and Schreier, H. J. (2003). Characterization of the microbial community and nitrogen transformation processes associated with moving bed bioreactors in a closed recirculated mariculture system. *Elsevier Science* , 215, 187-202.
- Tcholbanoglous, G. (2002). The Role of Decentralized Wastewater Management in the Twenty-First Century. *Water Environment Federation* .
- Thomsen, J. K., Geest, T., and Cox, R. P. (1993). Mass spectrometric studies of the effect of pH on the accumulation of intermediates in denitrification by *Paracoccus denitrificans*. *Applied and Environmental Microbiology* , 60 (2), 536-541.
- Vanotti, M., Szogi, A., and Vivies, C. (2008). Greenhouse gas emission reduction and environmental quality improvement from the implementation of aerobic waste treatment systems in swine farms. *Waste Management* , 28, 759-766.
- Wagner, M., Loy, A., Nogueira, R., Purkhold, U., lee, N., and Daims, H. (2002). Microbial community composition and function in wastewater treatment plants. *Kluwer Academic Publishers* , 665-680.
- Water Environment Federation (WEF). (1997). *Energy Conservation in Wastewater Treatment Facilities*. Alexandria, Virginia: Water Environment Federation.
- Whelan, C. (2009 1-June). *Preparing for a carbon market cap-and-trade market place*. Retrieved 2010 20-October from AllBusiness:
<http://www.allbusiness.com/government/government-procedure-lawmaking-legislation/12583542-1.html>
- Wik, T. (1999). Adsorption and denitrification in nitrifying trickling filters. *Water Research* , 33 (6), 1500-1508.
- Yamaguchi, K., Kawamura, A., Ogawa, H., & Suzuki, S. (2003). Characterization of nitrous oxide reductase from a methylotrophic denitrifying bacterium, *Hyphomicrobium denitrificans* A3151. *Journal of Biochemistry* , 853-858.

Ye, R., Haas, D., Ka, J., Krishnapillai, V., Zimmermann, A., Baird, C., and Tiejde, J.M. (1995). Anaerobic activation of the entire denitrification pathway in *Pseudomonas aeruginosa* requires Anr, an analog of Fnr. *Journal of Bacteriology*, 177 (12), 3606-3609.